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## NOTICE.

*Beginning with Vol. XVI., each article has a paging of its own : and the position of an article in a volume is indicated by the number placed at its head.*

*It is hoped that this arrangement, which enables us to print papers independently of one another, will ensure a more rapid publication of the material than has been possible heretofore.*

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## An Orographic Sketch of Korea.

By

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*With Plates I—IV.*

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### I. INTRODUCTION.

Korea is the Italy of Eastern Asia. It stretches out from the main body of Manchuria in a southerly direction between the *cul de sac* of the Yellow Sea and the Sea of Japan, both being fringing seas, as Italy projects between the Adriatic and the Mediterranean.

On the north and north-west the Korean peninsula is bounded by a well-defined topographic feature—the equatorial range of Chyang-päik-san, and a southerly-lying basin drained by the Amnok Gang<sup>1)</sup> and the Tu-man Gang. Similarly the peninsula of Italy is limited on the north by the Alps, and the plain of Po.

Both peninsulas stretch about 10 degrees meridionally ; Korea

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1) The *Yu-lu-Kiang* (鴨綠江) of the Chinese, signifies the *duck-green river* from some resemblance of the colour of the river-water to that of a duck's neck. The *Gang* or *Kang* (江) signifies in the Korean large, and *chhyön* (川), *mul* or *nai* (水) small streams.

from  $33^{\circ}$  N. lat. to  $43^{\circ}$  N. lat.; Italy from  $36\frac{1}{2}^{\circ}$  to  $46\frac{1}{2}^{\circ}$ . They lie, as we have seen above, in nearly the same latitude of the temperate zone, and enjoy an agreeable, transitional climate, neither too wet nor too dry. Both are inhabited by peoples of very ancient culture.

However similar in their general outlines, there are yet many points of dissimilarity, especially in regard to their internal geological components and structures, and their external land-forms. Italy is not wanting in young geologic formations, while Korea is in the main built up of Archæicum and Palæozoicum. Though both curve a little to the east, Korea is mountainous on the side of the Sea of Japan, and rather flat toward the Yellow Sea; while in Italy the Apennines run along the axis of the country.

This Asiatic Italy, fitly called by W.E. GRIFFIS the “Land of the Hermit Nation,” was secluded from the rest of the world for a long time, and even her old neighbours, the Japanese and the Chinese were strictly and vigilantly prevented from penetrating into the country. It is a unique patch of the earth’s surface, *terra incognita* in all respects, excepting eight free ports and the two inland towns, where over 20,000 Japanese and men of other nationalities have made themselves at home, but know nothing of what lies a few kilometers from them in the interior. Consequently, hitherto, only a few Westerners have made trips into the country, and studied the land and its people. Lately, I have twice made winter-journeys in the peninsula, in 1900-’01, and 1901-’02, extending over fourteen months. I spent 266 days in travelling over the interior in a caravan-like suite with six men and four ponies, daily marching nearly 20 kilometers, and covering altogether 6,300 kilometers or 1,575 *ri*. As will be seen on the annexed map, my routes ran nearly equidistant, crossing and recrossing the peninsula from one shore to the other, thus enabling me to get an idea of the general land-forms and



geology of the country, which were the main scopes of my two journeys.

As is well known, the outline of Italy is compared to that of a boot. That of Korea may be taken to represent a rabbit in a standing position with Chyöl-la Do<sup>1)</sup> for the hind legs, Chhyung-chhyöng Do for the anterior extremities, Hoang-hái Do and Ph्योंg-an Do for the head, and Ham-gyöng Do for the disproportionally large ear; Kang-uön Do and Kyöng-syang<sup>2)</sup> Do will then correspond to the shoulders and back.

The Koreans have their own fictitious representation of the outline of their country. The figure, they imagine, is that of an old man<sup>3)</sup>, his back bent with age, his arms folded in the attitude of paying paternal homage to China. They thought their country was by nature formed to be a dependency of the Middle Kingdom, and this notion drove its roots deep into the mind of the literary class, though it has been dispelled since the Sino-Japanese war of 1894-'95.

About Korea much has already been written from direct and indirect observations, but the descriptions of her land-features generally run in the same loose style in almost every work, without any principle based on the internal structure as manifested in the external topography. In my line of study I have only two names to mention, *viz.*, those of v. RICHTHOFFEN and Dr. C. GOTTSCHKE, whose works are,

1) The peninsula is divided into eight *Do* or departments, *viz.*, Hoang-hái Do (黃海道) Ph्योंg-an Do (平安道), Ham-gyöng Do (咸鏡道), Kang-uön Do (江原道), Kyöng-geui Do (京畿道), Chhyung-chhyöng Do (忠清道), Chyöl-la Do (全羅道), Kyöng-syang Do (慶尙道), the latter, three being collectively called the *Sam-nam* or the Southern Three.

2) In Korean geographical names the *y* is mute when preceded by *s*.

3) No doubt, Korea is also geologically a very old land, to which fact I shall frequently advert in the sequel.

however, highly significant, and served to give me a general idea of the geography and geology of the peninsula.

Referring to the principal mountain range the latter<sup>1)</sup> says from his own personal observation that it runs along the eastern coast. On the north, the range trends from S.W. to N.E. (a part of the Hyang-san)<sup>2)</sup>; in the middle from N.N.W. to S.S.E. (the Thai-Päik-san), and on the south from N.E. to S.W. (the Syo-Päik-san). In the north-western peninsula, there runs meridionally an independent ridge which shifts the course of the Am-nok Gang. Generally the geological axes are identical with those of the mountains, one exception to this general rule being a small ridge, the Myör-ak-san, which traverses Hoang-hăi Do at right-angles to the axis of the peninsula. The mountains owe their origin to two systems of earth-folds, and they never exceed the limit of 1,500 meters. In general the country is an extensive, but low mountainous land which approaches neither to the character of a plateau, nor that of a plain.—Thus far GOTTSCHÉ, who, it will be seen, has hit the mark so far as the fundamental elements of his topography are concerned.

In 1881, v. RICHTHOFEN<sup>3)</sup> had already spoken of two systems of mountains in Korea, from an inspection of a map. “At right-angles to the axial direction of Liau-tung,” he says, “a long extended arm juts out to sea, forming the peninsula of Korea. It is attached to the continent at the north-west corner, where the peninsula has its greatest breadth, and here starts a land of different character which governs nearly the half (north) of all Korea, and is drained by two rivers, *viz.*, the Am-nok and the Tu-man. If we should try to reconstruct mountain-chains from the net-work of rivers and the

1) ‘*Geologische Skizze von Korea.*’ Sitzungsberichte der Kön. Preuss. Akad. der Wissenschaften zu Berlin, XXXVI, Berlin, 1886.

2) *San* or *moi* (山) signifies mountains.

3) ‘*China.*’ II. S. 131.

sudden turn of their courses, the most prominent one of the chains would undoubtedly be that of the Chang-pai-shan<sup>1)</sup> (Kor. Chyang-päik-san), which is the prolongation of the axis of Liao-tung, namely, W.S.W. to E.N.E."

It is quite otherwise for the rest of the peninsula. The direction (N.N.W.—S.S.E.) of the highly-elevated, eastern coast led him to suppose the knee at Mao-êrh-shan<sup>2)</sup> of the Am-nok River was caused by the prolongation of the coast range which seems to penetrate far into the interior of the Nonni and Sungari regions. The existence of this old strike-direction in the gneisses of Shan-tung can be seen in some measure in the peninsular land-feature, though at later times the axis of folding in W.S.W. to E.N.E. became prevalent.

v. RICHTHOFEN'S wide experience in China, especially in Shan-tung, forces him to recognize this important tectonic line, which *I venture to call the Korean* in contrast to the Sinian. I will return to this Korean line in the sequel.

Korea had a good geographer a century ago, just as China had

1) Some confusion seems to exist in reference to the nomenclature of the sacred mountains on the border-land of Korea and Manchuria. The Manchus call the Ko-erh-min-Shang-chien-Alin (歌爾民商堅阿鄰). In old Chinese books they are named Chang-pai-shan (長白山), T'u-t'ai-shan (徒太山), or Pai-shan (白山). At present, people call them Lao-tai-shan (老大山) or old great mountains, Chang-alin or long mountains, on the Manchurian side. On the opposite Korean side, the natives speak of them as Chyang-päik-san (Long-white Mountains), Po-t'ai-san (Rich-great Mountains), or Thai-päik-san (Great-white Mountains). The meanings attached to these names are all the same, signifying white or long white mountains. The peoples from the Manchurian, as well as from the Korean side seem to make no distinction between the long range and the volcano upon it which is at the same time the culminating point of the range.

I look at and describe the border-mountains from the Korean side, and call the range itself the *Chyang-päik-san*, and the volcano *Päik-tu-san* or the White-head Mountain. It should be noticed that there is another Chyang-päik-san in northern Ham-gyōng Do, which should be distinguished by prefixing *Syo* (*Small*). Wängler remarks (*Die geographische Verbreitung der Vulkane*, 1901, S. 25.) that Krahmer (*Russland in Asien*, IV.) writes Pei-to-san (for the volcano) instead of Paischan, the former, Korean, the latter, Chinese. This remark is likely to produce further confusion.

2) 帽兒山, a Chinese military station.

many in former days. The book *Chyo-syön-phal-yök-chi*<sup>1)</sup> says: "The Kuen-lun system sends off the In-shan<sup>2)</sup> range, *etc.* eastward through the south of *shamo* as far as I-wu-lu-shan<sup>3)</sup>, where it is cut off by the plain of Liao-tung; but it again rises to Păik-tu-san, which is what is called the Pul-ham-san<sup>4)</sup> in the Buddhistic work *San-hăi-Kyöng*<sup>5)</sup>. From Păik-tu-san one ridge branches off northwards to Ninguta, while the right arm stretches southwards under the name of the *Korean Range*."

"This Korean Range starts from the before-mentioned Păik-tu-san, the sacred shrine and cradle of the Koreans, towards the coast-ridge—the Syo-Chyang-păik-san<sup>6)</sup> of northern Ham-gyöng Do. It turns to the S.W. from the free port of Syöng-jin still following the coast, then southwards from Ham-heung, and is linked to the chains of Thyöl-lyöng<sup>7)</sup> of Wön-san, Keum-gang-san<sup>8)</sup> or the Diamond Mountains, and then to Thai-Păik-san<sup>9)</sup> at the north corner of Kyöng-syang Do. While the last-named proceeds straight along the coast, one ridge shoots off to the S.W. under the general name of the Small or Syo-Păik-san, forming the boundary with Chhyung-chhyöng Do on the N.W. In its course, one ridge is again detached to the S.W. at Tög-yu-san<sup>10)</sup> from the main stem, which traverses obliquely Chyöl-la Do, and reaches Hăi-nam, finally emerging in the island of Chyöi-jyu (Quelpart), off the south coast of the same province."

"Thus the main ridge runs along the east coast, forming the well-pronounced water-parting, so that most of the large rivers empty into the Yellow Sea, while the short and rapid streams all flow down to the Pyök-hăi or Blue Sea (the Sea of Japan). Between the

1) The author of this book (朝鮮八域誌) was I-Chyung-hoan (李重煥).

2) 陰山.

3) 醫巫闾山.

4) 不咸山.

5) 山海經.

6) 小長白山.

7) 鐵嶺.

8) 金剛山.

9) Thai or Great Păik-san (太伯山).

10) 德裕山 at the junction of three provinces.

Thai-Päik-san and Syo-Päik-san ranges, however, the Nak-tong Gang<sup>1)</sup> and Syöm-jin Gang<sup>2)</sup> discharge their waters into the southern sea."

The above statement of the Korean geographer is in the main correct. If v. RICHTHOFEN had read Ts description with the late HASSENSTEIN's map<sup>3)</sup> of Korea in hand, he could doubtless have drawn a good picture of the orography of the peninsula in his "*China*", or "*Morphologischen Studien aus Ostasien*," from his wide experience and deep knowledge of Eastern Asia.

## II. NORTH AND SOUTH KOREA.

Before entering upon the subject proper, I will first of all speak of its two main divisions. If a line be drawn obliquely through the peninsula from Chyo-syön Bay (Broughton Bay) on the north-east to Kang-hoa Bay<sup>4)</sup> near Ché-mul-pho<sup>5)</sup>, it will nearly coincide with the neck of the imaginary rabbit, and will divide the peninsula<sup>6)</sup> approximately into two equal halves. The part lying to the north-west of this line comprises three departments of Ham-gyöng Do, Phyöng-an Do, and Hoang-häi Do. The corresponding south-eastern half includes the remaining five departments of Kyöng-

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1) 洛東江.

2) 鎭津江.

3) Petermann's Geographische Mittheilungen. Jahrgang 1883, Tafel 10.

4) 江華灣.

5) 濟物浦.

6) The area of the peninsula is 218,650 sq. kilometers. With Italy, Japan, and Manchuria it is in the following proportions: 1: 1.3: 1.7: 4.3.

geui Do, Kang-uön Do, Chhyung-chhyöng Do, Chyöl-la Do, and Kyöng-syang Do. *I venture to call the former North and the latter South Korea.* This dividing line is not only convenient for *descriptive purposes*, but is almost a natural boundary.

*Firstly*, because it is the boundary of historical development. The north is the land of Keui-chǎ Chyo-syön,—the oldest dynasty of Chinese origin, founded by Keui-chǎ<sup>1)</sup> (B.C. 2317). This was succeeded by the second Chyo-syön,—the dynasty<sup>2)</sup> of the Ui family (B.C. 209—107). Having been for a while amalgamated with the Chinese Empire (the Han dynasty), it had fallen into the hands of the Pu-yö<sup>3)</sup> invaders, who called the country Ko-ku-ryö<sup>4)</sup> (B.C. 36—A.D. 672). These kingdoms had their rise and fall in the northern peninsula, and a part of Manchuria, or at their greatest their south boundary was the river Han, which flows through the heart of Kyöng-geui Do, and near the bank of which is situated the present capital Seoul (Han-syöng)<sup>5)</sup>.

In short, the north is the old Chyo-syön, while the south was little known during these early periods. Later, there had arisen in South Korea about B.C. 209 the Three Hans, *viz.*, Sin-Han<sup>6)</sup>, Pyön-Han<sup>7)</sup>, and Ma-Han<sup>8)</sup>. From the first two had sprung up in Kyöng-syang Do the Kingdom of Sil-la<sup>9)</sup> (B.C. 57—A.D. 936), and from the last, Päk-chyöi<sup>10)</sup> (B.C. 17—A.D. 660).

It was only in still later times that the whole peninsula was united under the one government of Ko-ryö<sup>11)</sup> or Korea (918—1392), which was replaced by the present I-family, the last Chyo-syön. With the rise of a new dynasty the name of the government is alter-

1) 箕子

2) 衛氏

3) 扶餘

4) 高句麗

5) 漢城(徐苑)

6) 辰韓 Chyöi-Han in Gale's *Korean-English Dictionary*, 1897.

7) 辨韓

8) 馬韓

9) 新羅

10) 百濟

11) 高麗

ed, and at the same time that of the country, just as is the case in China. The five-hundred years' existence of the I-family terminated in 1898, since which time the peninsula has gone under the name of *Tai Han*<sup>1)</sup>.

*Secondly*, because the dividing line is the line of the least elevation of the land. Nowhere else do we find an easy path from the Sea of Japan to the opposite shore. The only passes from the free port of Wön-san viâ Seoul to Ché-mul-pho are the Thyöl-lyöng<sup>2)</sup> and Chyuka-ka-ryöng<sup>3)</sup>, the first being situated on the east of the latter, and both being not far from Wön-san; we have to choose one of them for an overland route. The so-called Chyuk-ka-ryöng road has a marked topographic feature. It is a *rift valley* or *Graben* obliquely crossing the geological strike. From the top of Nam-san in Seoul, we see on the east a regular cliff with its escarpment toward us. It runs from the mouth of the Keum Gang<sup>4)</sup> to the head of Wön-san harbour, and the well-fortified castle of Koang-jyu<sup>5)</sup>, 12 kilometers from the capital, stands on its edge. *I call this the Koang-jyu ridge.* The *other* ridge starts from the Ma-sing-nyöng<sup>6)</sup>, the highest pass of 1020 meters (the second pass A-ho-bi-nyöng being 760 meters), between Wön-san and Phyöng-yang, and lowers at the mouth of the In-jin Gang<sup>7)</sup>. The Ma-sing-nyöng ridge turns its fault-scarp to the east, making the counterpart of the Koang-jyu ridge, thus forming the trench-fault. Great basalt flows occurred at the end of the Tertiary, filling up the bottom and now forming the sterile plain of Thyöl-nön<sup>8)</sup> or iron plain, so named from some resemblance of the lava to magnetite. The Chyuk-ka-ryöng road goes gradually up this

1) 大韓

2) 鐵嶺. *Ryöng, lyöng, or nyöng* (嶺), and *koñi, kogñ* or *hyön* (峴), often affixed to local names, signify mountain-pass.

3) 竹駕嶺.

4) 錦江

5) 廣州

6) 馬息嶺.

7) 臨津江

8) 鐵原

lava-field, frequently crossing the canyon-like river-channel, and suddenly descends to Wön-san at the above-named pass, which is the edge of the basalt-mesa and the boundary of two provinces.

*Thirdly*, because this dividing line corresponds approximately to that of the climate. North Korea in this respect Manchurian, while the South is Japanese. The coast in the north is ice-barred for 3 months from the beginning of December. Even the south coast of Hoang-hăi Do is ice-barred as I have seen near Hăi-jyu<sup>1)</sup>, while Ché-mul-pho, though not far off, is never frozen up. However, the coast of Ham-gyöng Do is comparatively warm as far as the mouth of the Tu-man Gang, and the shore is open during the whole year. While I was travelling, I counted the days warm, when temperature rose to  $-5^{\circ}\text{C}$ . During three winter months I did not see the naked ground, and my caravan marched mostly on the smooth, frozen rivers, covered with fresh snows, especially on the Am-nok Gang. The average temperature at 6 a.m. in North Phyöng-an Do is  $-20^{\circ}\text{C}$ .

A great contrast with the above conditions is presented by the climate of South Korea. I made a journey in this region during the winter-months of 1900-'01, so that I am able to make a comparison. Mountain-tops in the interior are capped with snow from December to February, but the rivers are frozen for only a few days. As we proceed south-east across mountain-ridges which trend from N.E.—S.W., that is to say, in the Sinian direction the climate becomes gradually warmer. Fusan<sup>2)</sup>, therefore, enjoys a mild climate, comparable with that of northern Kyushu of Japan which lies opposite.

*Fourthly*, because in respect to topography, North Korea is mountainous. The belt of land between the Chyang-păik-san range

1) 海州.

2) August, the hottest month of the year has an average temperature of  $26^{\circ}\text{C}$ ., and the other extreme, January  $7^{\circ}\text{C}$ . The mean annual temperature is  $16.9^{\circ}\text{C}$ . Snow falls only about once a year.



and the line drawn from the mouth of the Chhyöng-chhyön Gang and Ham-heung is the Kai-ma<sup>1)</sup> plateau. It embraces the northern halves (West and East Kai-ma) of Phyöng-an Do and Ham-gyöng Do. The Ham-gyöng Do portion is on average 1,000 meters high, that of Phyöng-an Do 600 meters. The plateau may without hesitation be compared with the Great Khingan (*Hsing-an*) and Inner Mongolia. South Korea on the other hand abounds in hills interspersed with plains.

*Fifthly*, because in consequence of the climatical and orographical conditions, the south is rich and fertile, producing the rice, the main staple of the country and hence being the granary of the peninsula. Various kinds of tall bamboos, which play an important rôle in household economy are only grown in the south. Their northern limit of growth, which is also that of the *Camellia Japonica*, is the oblique line drawn from the free port of Kun-san to Ul-chin at the south corner of Kang-uön Do.

*Sixthly*, because the physique and temper of the inhabitants differ in both halves. A Korean proverb says of the southern men and the northern women “*nam nam penk nyö*”, meaning that they are in bodily appearance more attractive than their respectively opposite sexes. The southerners are light-hearted and cunning, the northerners are silent and obstinate.

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1) Kai-ma (蓋馬), one of the provinces of China before the Ku-ryo dynasty.

## III. OROGRAPHY.

The fundamental features of the topography of Korea, as in other lands, are the result of internal geologic structure. Indeed the peninsula was the battle-ground of earth-movements of two directions—the *Sinian* and the *Liau-tung*. In the south of the lava-drowned rift-valley of Chyuk-ka-ryöng, already mentioned, the axes of crust-folds are mainly N.N.E.—S.S.W., *i.e.* the *Sinian*. In the extreme north (in the Kai-ma plateau), the fold-mountains run from W.S.W. to E.N.E. in the *Liau-tung* direction. The earth-movements had folded the core of gneiss-granite together with the overlying mantle of normal gneiss and mica-schist. The kernel of South Korea is the wedge-shaped massive of Chi-ri-san at the boundary of Chyöl-la Do and Kyöng-syang Do. That of the north is also the wedge-shaped massive of Kai-ma Land. These *Sinian* and *Liau-tung* massives, together with their overlying mantles meet each other with their apices, and struggle for the supremacy in north-eastern Ham-gyöng Do, thus leaving between them the third wedge of low neutral land.

Therefore, the peninsula is divisible orographically into 3 gigantic wedges. The south, embracing the whole of South Korea, is the old land of The Three Hans. North Korea is again divided into the Kai-ma plateau, and the *intersertal* wedge,—the land of old Chyo-syön or Paleo-Chyo-syön.

I have still to mention a *third element*. This time the earth-movement did not produce folds, but ruptured and dislodged the crust, tilting up the edge. The main edge runs N.N.W. to S.S.E., at the margin of the Sea of Japan, facing its high scarp to the deep shore. This tectonic disturbance, relatively of young age, produced prominent ridges which constitute the backbone and determine the present topography. The outline of the peninsula is due in

a great measure to this geological event. The block-edges I call collectively the *Korean Range*.

Having given this general skeleton, let me now proceed to details.

## A. THE HAN LAND<sup>1)</sup>.

South Korea is the land of the First Three Hans (B.C. 209—57), where the petty kingdoms led a very troublesome, ephemeral existence, waging among themselves never-ceasing war for the political ascendancy. Sin-Han (cap. Kyōng-jyu), and Pyōn-Han (cap. Kim-hǎi) occupied the present Kyōng-syang Do, and from them later sprang up the Kingdom of Sil-la (cap. Kyōng-jyu, A.D. 57—926). Ma-Han (cap. Ik-san) had its home in Chyōl-la Do, Chhyung-chhyōng Do, and a part of Kyōng-geni Do, and developed into Sil-la's rival, Pǎik-chyōi (caps. Chik-san, Koang-jyu, modern Seoul, Ung-jin, and Pu-yō, B.C. 17—A.D. 660<sup>2)</sup>). The natural boundary of Kyōng-syang Do with the two western Do lies in the Syo-Pǎik-san range, and their ruined castles are still to be seen at the foot of the mountain-passes. We now return to the subject of orography.

### a. THE SINIAN SYSTEM.

Starting from the free port of Mok-pho, and following up the

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1) By the Han-land or the Three Hans, I mean the First Three Hans, viz., Ma-Han (馬韓), Pyōn-Han (弁韓), and Sin-Han (辰韓). It must be understood that there were the Second Three Hans, arisen at later times. They were Sil-la (新羅), Pǎik-chyōi (百濟), and Ko-ku-ryō (高句麗), the latter embraced the whole North Korea, besides a part of southern Manchuria. I must also call the reader's attention not to confound Ko-ku-ryō (高句麗) of Pu-yō tribe with *Ko-ryō* (高麗). They were quite different dynasties that had existed in North Korea, the former being older. To avoid confusion, the former should better be called *Ku-ryō* (B.C. 36—A.D. 672), and not *Ko-ku-ryō*. From Ko-ryō (918—1392), the present European name Korea is derived.

2) Their struggles were the cause that led Japan to make the acquaintance of Korea in former days, in complying with the earnest request of one of these rivals for armed help. In return, the Koreans introduced the Chinese civilization into Japan.

Yöng-san Gang north-eastward through the plain of Na-jyu<sup>1)</sup>, Koang-jyu<sup>2)</sup>, Tam-yang<sup>3)</sup>, and Syun-chhyang<sup>4)</sup>, we then turn to the north and proceed to Seoul through the plain of Chyön-jyu<sup>5)</sup>, the town of Kong-jyu<sup>6)</sup>, across the Keum Gang<sup>7)</sup>, and the plain of A-san<sup>8)</sup>, to the capital. This route passes through the wealthiest and most populous districts. Besides, we have to cross *two ridges* on the way.

a) The *first ridge* lies between Syun-chhyang and the general magisterial town Chyön-jyu, and this is *No-ryöng*<sup>9)</sup>. From Nam-uön<sup>10)</sup> to Chyön-jyu, the road crosses the same ridge a little to the east,—Man-ma-koan<sup>11)</sup>. This is a fold-mountain of normal gneiss, granite-gneiss and mica-schists, with the axis trending from S.W. to N.E. I consider this to be a *member of the Sinian System* which is typically folded in Fokien and neighbouring provinces in South China. Pumpelly<sup>12)</sup> says that “a line drawn from near Canton, and passing through the Chusan archipelago, will represent the mean trend of the coast range (of China), and, if prolonged to the N.E., it will cut the Korean peninsula near its southern end.” I have simply to corroborate his wide-reaching assertion. It is very remarkable to see that in modern writings about Korea Pumpelly’s opinion on this point is consigned to oblivion.

The No-ryöng range disappears in the Ssang-chä<sup>13)</sup> group of islands off the coast of Mok-pho, where still the forms of islets bespeak its natural connection. Each and every islet of the group appears like a shark’s tooth projecting from the surface of the sea; as a group they are arranged in the Sinian direction. To the north-

1) 羅州.

2) 光州.

3) 潭陽.

4) 淳昌.

5) 全州.

6) 公州.

7) 錦江.

8) 牙山.

9) 蘆嶺.

10) 南原.

11) 萬馬關.

12) “*Geological Researches in China, Mongolia, and Japan*,” p. 2. Smithsonian Contribution to Knowledge, 1866.

13) 雙子巖島.

east, the No-ryöng runs with its steep side towards the north-west till it reaches the Chhyu-phung-nyöng<sup>1)</sup> pass at the boundary of three provinces, where the projected Fusan-Seoul Railway will cross the highest point of the line (only 200 meters !). In Kyöng-syang Do, it is cut down to the east by the Syo-Päik-san<sup>2)</sup> whose tilted edge runs obliquely to the No-ryöng from N.N.E. to S.S.W., culminating at the Chi-ri-san massive on the south, and terminating near the shore of Kang-neung<sup>3)</sup> in southern Kang-nön Do. This Syo-Päik-san is one of the most important topographic elements in South Korea, separating Kyöng-syang Do on one hand from Chhyung-chhyöng Do and Chyöl-la Do on the other.

The old No-ryöng fold, after being submerged under the Kyöng-syang<sup>4)</sup> formation, and further invaded by a gigantic laccolite of granite, reappears at Ul-chin<sup>5)</sup> in the south corner of Kang-nön Do, still keeping its former strike-direction. This granitic area usually called the Thai-Päik-san<sup>6)</sup> region embraces about 4,000 square kilometers. It is a tree-less tract, and the biotite-granite of the post-Permo-Triassic age is fast falling into ruins and disintegration through the action of the atmospheric agencies so as to be almost base-levelled into peneplain. The entire aspect of the country is dreary and desert-like. It is labyrinthic with rolling naked hills, and flat valley-bottoms are drowned in loose sand. The ground is dry and clean. It is the Seoul region of the south. Though we were here in the heart of Kyöng-syang Do, my barometer showed an altitude of but 150 meters, and a little to the west only 60. From Mun-gyöng<sup>7)</sup> to the mouth of the Nak-tong it is 200 kilometers with a gradient of only 60 meters. The region is, therefore, a depression by denudation. We shall see

1) 秋豐嶺

2) 小白山

3) 江陵

4) It is possibly of the Permo-Triassic age.

5) 蔚珍

6) 太伯山

7) 聞慶

hereafter such *erosion hollows* in many parts of Korea, always in *granitic districts*.

*The No-ryöng range, so far as we have seen, is a fold-mountain, and is the oldest and the southernmost range of the Sinian system in the whole peninsula.*

β) After passing Chyön-jyu<sup>1)</sup>, and Kong-jyu, and crossing the Keum Gang northwards to Seoul, we have to ascend the pass of *Chhya-ryöng*<sup>2)</sup> to On-yang-do<sup>3)</sup>. Broadly speaking, it is a synclinal ridge of mica-schist mantle upon gneiss. It probably commences in the Heuk-san Group<sup>4)</sup> in the Yellow Sea, and runs through a group of islets off the free port of Kum-san<sup>5)</sup>. It then enters Chhyung-chhyöng Do, and makes the above-named Chhya-ryöng pass. It is much disturbed on the north-east by the intrusions of large masses of microgranite and granite-porphry.

The mica-schists disappear in the heart of Kang-uön Do, being replaced by shallow folds of granite-gneiss, which are sharply faulted in the *Tai-koal-lyöng region*<sup>6)</sup> between Kang-neung and Ko-syöng<sup>7)</sup>, still keeping the original direction of strike. The folded ridge, which has been traced thus far, I call collectively the *Chhya-ryöng range*, which trends from N.N.E. to S.S.W. *It is the second of the geological line, belonging to the Sinian System.*

The whole complex is cut down obliquely by the already-mentioned Koang-jyu fault towards the north-west.

The No-ryöng and the Chhya-ryöng ridges are both of the Sinian System and are old earth-folds. On account of their

1) The word *jyu* (州), affixed to local names, always signifies a magisterial town of the first class, enclosed in stone-walls.

2) 車嶺.

4) 黑山叢島.

6) 大關嶺.

3) 溫陽渡.

5) 群山港.

7) 高城.

high antiquity, they are now reduced into stumped and well-nigh subdued mountains. Therefore, they cannot be recognized as ridges in a topography, though they still mark distinct water-partings.

## b. THE KOREAN SYSTEM.

Another element which I have already treated in part, is the *Korean System*. This time the result of tectonic disturbance is not an earth-fold, but the *rupture* and *dislocation*. As this system originated at a somewhat later date than the preceding, probably post-Perm-Triassic, it has had a great effect upon the modern topography of not only South Korea, but also the whole peninsula; and not only on land-forms, but also on coast lines. We have to distinguish several members of somewhat diverse orientation in the system. I shall speak at first of the most important of these members.

### a) THE THAI-PÄIK-SAN RANGE.

i. *Median Ridge*.—From Ta-thai-pho point<sup>1)</sup> at the mouth of the Nak-tong Gang<sup>2)</sup>, a meridional ridge of green porphyrite and granite with fault-scarp facing east, runs through Ōn-yang<sup>3)</sup> and Kyōng-jyu<sup>4)</sup>, Chhyōng-syong<sup>5)</sup> and Yōng-yang<sup>6)</sup>, where the rocks are replaced by alternating beds of green tuffs and red shales. In the last-named district, the ridge intersects the No-ryōng range in granite-gneiss, and culminates near the Sa-gil-lyōng<sup>7)</sup> pass at the crescent-shaped, and tree-covered *Thai-Päik-san*<sup>8)</sup> of Paleozoic rocks (1,500 m.). The name of this mountain is known to every Korean and is regarded with some reverence, though the high peak itself presents to us no specially

1) 多太浦鎮.

2) 洛東江.

3) 彦陽.

4) At Chhyōng-gyōng-kokāi (淸鏡峴) it lowers to 200 meters.

5) 靑松.

6) 英陽.

7) 沙吉嶺.

8) 太伯山.

fantastic shape. *Hereafter I shall call the ridge, now under consideration, by this name.*

The Thai-Päik-san ridge sharply cuts off in the mountainous district of Sam-chhyök, the tilted edge of the Syo-Päik-san which equally faces eastwards with fault-scarps. The ridge now deflects a little westwards and continues through O-däi-san, noted for its pagodas, to the famous Keum-gang-san, terminating at Thong-chhyön, after pursuing a lengthy course of 480 kilometers. The cliff between Chyang-chyön Cove and Thong-chhyön fully exposes an oblique profile of the ridge, and detached elods of granite of monstrous shapes are seen in the sea retaining the former direction of the ridge. Scenery lovers of Korea frequent the shore and native-geographers style these islets the *Häi-Keum-gang* or Mid-sea Diamond Mountains.

Keum-gang-san or the Diamond Mountain (1,200 meters) is a large granitic stock, stretching north-south and penetrating Paleozoic rocks. It is excavated to its bottom by a crooked, canyon-like gorge, the precipitous wall overhanging the bottom and raising a multitude of grotesque heads; hence to the mountain not unusually the appellation of Twelve Thousand Peaks<sup>1)</sup> is given. The valley bottom and steep slope are forested with pine, the *Pinus pinea*, and maples, through which clear water rushes down in thousands of cataracts<sup>2)</sup>. About fifteen pagodas large and small have been here since the Sil-la period, some perched on rock heads, some buried deep in the forest giving shelter to world-renouncing monks and nuns. It is the Yosemite of Korea, and a favourite resort of Westerners.

ii. *Coastal Ridge*.—The Thai-Paik-san is really triple in structure; the one hitherto spoken of, is the middle and highest line. There is *another* lying to the east and parallel to the first, and this is

1) 一萬二千峰

2) Man-phok-dong (萬瀑洞) or ten thousand water-falls.



similar in structure throwing down the *right* block directly to the level of the sea. The precipitous wall which we see landwards from the sea is the scarp of this easternmost fault. A belt of block interposed between the first and second ruptured planes often slants steeply landwards.

A *third structural line* is seen to run to the west and nearly parallel to these two lines, this time throwing down the *west wing*, and this movement creating the inland scarp-ridge. The Thai-Paik-san range resulted literally, in the geological language, from step-faults, and the whole stretch is a crust-block or *Horst*. I shall now trace the maritime ridge.

The *sea-board ridge* starts by the name of Tong-tai-san<sup>1)</sup> from Yöm-pho<sup>2)</sup> (Tikhmenef Point) near Ul-san<sup>3)</sup> cove, which is an inlet of the *rias* type. The coast between the harbour of Fusan and the cove of Ul-san was 300 years ago the landing place of the Japanese army under Hidéyoshi. The Tong-tai-san and its northern prolongation are a tilted block uplifted on its east side, slanting westwards; and remarkably granitic patches are seen between this and the median ridge, presenting the characteristic form of granitic mountains within an area of green rocks. The coastal ridge also marks the boundary of light-coloured rhyolite and its derivative sedimentaries of the Tertiary age. The shallow Yöng-il<sup>4)</sup> (Unkofsky Bay) is within this geological formation. The ridge then proceeds northwards through Yöng-häi<sup>5)</sup>, and Ul-chin<sup>6)</sup>. Sim-ni-kokäi<sup>7)</sup> and Nölp-chhi<sup>8)</sup> are the passes leading to the inland plateau.

The coastal escarpment goes on along shore through Kang-uön Do as far as Ko-syöng, where it is cut short at Chyang-chyön Bay

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1) 東大山

2) 迎日灣

3) 十里峴

4) 驪浦

5) 寧海

6) 廣峙

7) 蔚山

8) 蔚珍

near the Mid-sea Diamond Mountains. The *pass of Tai-koal-lyöng* west of Kang-neung is the ascent to this edge, and I was in the habit of noting down in my diary the whole coastal ridge by this name. It, however, lowers at the north of Syöl-ak-san<sup>1)</sup>, becoming again steep and high at the before-mentioned Diamond Mountain, whose maritime escarpment is nothing more than this ridge. The coves of Ul-san and Chyang-chyön are the two inlets at both ends. There is a space left, 4-8 kilometers wide, between the ridge and the shore all along the harbour-less coast. This long belt of 400 kilometers is a low hilly foreland, excepting in the Sam-chhyök<sup>2)</sup> district where it is rocky, as the Syo-Paik-san ends at the sea.

The Kang-uön Do portion, north of Kang-uön was in former times called the land of Yöi<sup>3)</sup> or barbarians<sup>4)</sup>, at later times the name was changed to Myöng-jyu<sup>5)</sup> or the Maritime province. There is no other part of the peninsula the past history of which is so little known as that of this poor, obscure district, and this is solely due to its peculiar geographical situation. The only easy way that leads to the maritime region from the interior is the one going up along the Ku-mi Gang<sup>6)</sup>, an upper tributary of the Han river, from the general magisterial town Chhyun-chhyön<sup>7)</sup> via In-työi<sup>8)</sup>.

iii. *Inland ridge*.—This is one of the elements of the triple structure of the Thai-Päik-san, and the line of dislocation marks the western limit of the mountain, throwing down the *west* side to a lower level. The said line runs nearly through the middle of Kyöng-syang Do, and creates the meridional basin of the Nak-tong Gang, the western elevation being the often-cited Syo-Päik-san ridge on the boundary of the province. Though the scarp has no pronounced

1) 雪岳山.

2) 三陟.

3) 穆國.

4) The Koreans are calling savages *Orangkai*.

5) 溟州.

6) 九棍江.

7) 春川府.

8) 麟蹄.

effect on the step-land scenery as in the case of the sea-board ridge, yet I believe I have seen many knife-cut edges during my traverses across the interior plateau, 300 meters high.

The Inland Ridge seems to start from Kō-chyōi<sup>1)</sup> in the southern archipelago, and crossing a channel to Thyōn-chǎ-bong<sup>2)</sup> of Ung-chh-yōn<sup>3)</sup> it passes over the deflected course of the Nak-tong Gang at Sam-rang-jin<sup>4)</sup>. Then it goes by Mil-yang<sup>5)</sup> and Chǎ-in<sup>6)</sup>, and Ha-yang<sup>7)</sup> and Eui-syōng<sup>8)</sup>, at the last village I saw this low but sharp ridge of green tuff and red shale, having the appearance of quite a fresh dislocation. The ridge is seen also east of Pong-hoa<sup>9)</sup> in the granitic Thai-Pǎik-san region, and after deflecting to the west it penetrates into the little known area of Paleozoic terrane of the upper Han river. I have crossed it at Tai-hoa<sup>10)</sup> on the Tai-koal-lyōng road, and it passes west of In-tyōi which is located in a depression between this and the Median ridge. Again I have crossed the same ridge midway between Chhyang-do and the Diamond Mountain at Kan-bal-ko<sup>11)</sup>, where it trends N. 30° W., and terminates at the entrance of Wōn san harbour.

*Another ridge* of similar structure, lying to the west of the above-named, seems to begin at the head of Ma-san-pho<sup>12)</sup>, and proceeds by Chhil-ŭn<sup>13)</sup>, Yōng-san<sup>14)</sup>, Hyōn-phung<sup>15)</sup>, Chhil-kok<sup>16)</sup>, and Pi-an<sup>17)</sup>, along the east side of the Nak-tong Gang. This should be called the *Ma-san-pho Ridge*.

- 1) 巨濟島.
- 3) 熊川.
- 5) 密陽.
- 7) 河陽.
- 9) 奉化.
- 11) 干發告.
- 13) 漆原.
- 15) 玄風.
- 17) 比安.

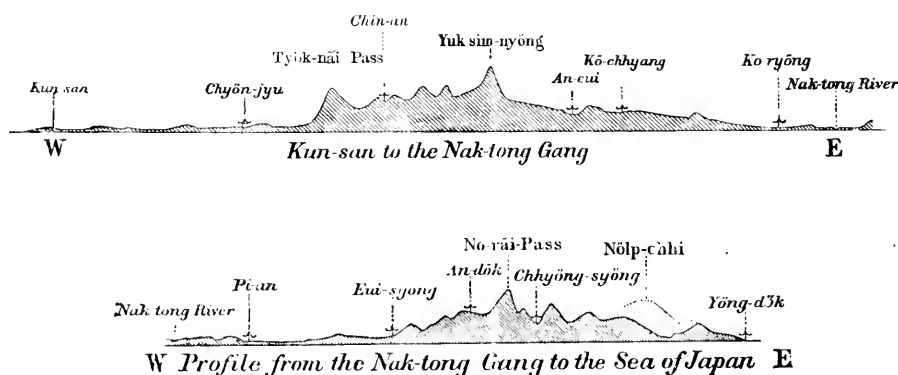
- 2) 天子峰.
- 4) 三浪津.
- 6) 慈仁.
- 8) 義城.
- 10) 大和.
- 12) 馬山浦 or 馬浦 (Mapho).
- 14) 靈山.
- 16) 漆谷.

There are still *two other ridges* of similar structure and the same orientation, but of short extent, and topographically insignificant. They all lie on the *west side* of the Nak-tong Gang.

So much for the ruptured ridges which constitute the Thai-Päik-san Mountains.

### β) THE SYO-PÄIK-SAN RANGE.

The Korean System in South Korea comprises a considerable number of ridges which, so far as they have come under my observation, are all of tectonic blocks, and are separable into two groups. I have already given characteristics of a group which is provisionally called the Thai-Päik-san Range. As will be seen in the foregoing pages, the approximate trend of its members is N.N.W. to S.S.E., conforming to the general form of the coast of southern Korea, which form has an intimate genetic relation to the direction of the mountains.



Scale 1:750,000. Vertical  $\times 2$ .

**Figs. 1 and 2.**—The two are really a continuous profile of the Han Land or South Korea from the west to the east across Chhyung-chhyöng Do and Kyöng-syang Do, traversing on the way the Syo-Päik-san Range from Työk-näi Pass to Yuk-sim-nyöng (690 m.) in the above, and the Thai-Päik-san Range between Eui-syöng and Yöng-dök in the lower figure. The Syo-Päik-san in Fig. 1, marks the boundary of two provinces, forming at the same time the watershed between the Keum-Gang and the Nak-tong-Gang, the former discharges its waters to the Yellow Sea at the free port of Kun-san, the latter empties into the sea near the Japanese colony of Fusan.

The one, now under consideration, is distributed in the middle of the peninsula, and is usually designated the *Syo-Päik-san Range*. It has already been spoken of in connection with the No-ryöng fold which it cuts off, and farther north it seems in turn to have been intersected by the Thai-Päik-san members. About the last point, I am in some doubt, for, my route did not traverse the mountainous part of Sam-chhyök on the east coast to Thai-Päik-san, nor to Chyöng-syön<sup>1)</sup> over the pass of Päik-pöng-nyöng<sup>2)</sup>.

It was said that there the mountains were rough and ponies could scarcely be employed at that time. Consequently my personal knowledge unfortunately does not enable me to give details as to how the Thai-and Syo-Päik-sans intersect each other, and as to which took the active part. It is, however, likely that it is the latter that was severed in its north-easterly course by the former.

I do not even know whether the Syo-Päik-san in this region is a fold-ridge, or a tilted edge of Paleozoic formation. Judging, however, from the structure seen at Tyo-ryöng<sup>3)</sup> and I-hoa-ryöng<sup>4)</sup> (520 meters) on the high way between Seoul and Fusan, we shall probably see at the junction the Syo-Päik-san in the first form. The pass of Tai-chyung-nyöng<sup>5)</sup>, 500 meters high, between Tan-yang<sup>6)</sup> and Phung-geui<sup>7)</sup> exposes a granitic base capped by a Paleozoic bed of slate and limestone dipping to the northwest, and shows the igneous rock to be of a laccolitic nature. Syo-Päik-san in a narrow sense is really the edge of this Paleozoic complex of the Chyung-nyöng pass.

A large triangular area of granite, which the Koreans call the Thai-Päik-san region, is situated at the inner angle of the Thai-and Syo-Päik-sans. Analogous cases are frequently mentioned in geol-

1) 旌善.

2) 白復嶺

3) 烏嶺.

4) 伊火嶺

5) 大竹嶺

6) 丹陽

7) 豐基.

ogical literature, and granite and other eruptives are apt to seek their way to such geologically weak points.

i. *Hoang-chhi Ridge*.—This begins probably at Phyöng-san-pho<sup>1)</sup> in Nam-hăi Island<sup>2)</sup> in the Southern Archipelago, and passing the narrow channel of No-ryang<sup>3)</sup> to the peninsula proceeds northwards through the passes of Hoang-chhi<sup>4)</sup> west of Chin-jyu<sup>5)</sup>, Chhyöng-möri-kokăi<sup>6)</sup> (360 m.) east of San-chhyöng<sup>7)</sup>, then Koan-bin<sup>8)</sup> (750 m.) west of Ko-ryöng<sup>9)</sup>, terminating in the isolated castle mount of Keum-mu<sup>10)</sup>. It is the *easternmost* of the members, marking the boundary of gneiss-granite and the Permo-Triassic formation.

The scarp is no doubt due to faulting, the dislodged part of gneiss dipping against the wall, as in the case of the coastal ridge of the Thai-Păik-san. Though not a very high ridge, yet its sharp escarpment is clearly visible from the top of Chhyöng-möri-kokăi. The wall-like precipice beyond the rolling hills (on an average 70 meters) of the Permo-Triassic region seen from the east bank of the Nak-tong Gang, is the one we have just traced. It is the landmark of this region.

ii. *The Phal-hyöng-chhi Ridge*<sup>11)</sup>.—Next to and lying to the west of the preceding, the ridge runs through the small peninsula of Yö-syu<sup>12)</sup>, the Pan-syöng pass<sup>13)</sup> and the grotesque Ök-kul-bong<sup>14)</sup>, of Koang-yang<sup>15)</sup>. Beyond the Syöm-jin Gang<sup>16)</sup> it enters the highest Chiri-san<sup>17)</sup>, then the Phal-hyöng-chhi pass (430 m.), Hoang-syök-

1) 平山浦.

2) 南海嶋.

3) 露梁.

4) Hoang-chhi or Hoang-tai-chhi (黃峙 or 黃大峙), 280 m. high.

5) 晉州.

6) 尺首峴.

7) 山淸.

8) 勸賓.

9) 高靈.

10) 金無山城.

11) 八兄峙脈.

12) 麗水.

13) 盤城峴.

14) 億窩峯.

15) 光陽.

16) 蟾津江.

17) 智異山.

san<sup>1)</sup> of Kō-chhyang<sup>2)</sup>, finally being cut short at Tōk-tai-san<sup>3)</sup> near the Chhyu-phung-nyōng pass. This is the highest ridge and forms the boundary of two provinces.

At the recess and foot of Chiri-san several pagodas are found, one of them being Ssang-gyōi-sǎ<sup>4)</sup>, and the intermontane valleys are infested with hordes of hungry bandits. The Chiri-san region, presenting the characteristic granitic scenery, is one of the *four celebrated mountains in Korea*, that are adorned with pagodas, the other three being Ku-uōl-san<sup>5)</sup> of Hoang-hǎi Do, Hyang-san<sup>6)</sup> of Phyōng-an Do, and the oft-mentioned Diamond Mountains of Kang-uōn Do, all granitic mountains.

The massives, lying to the east of this axial ridge, people call the Chiri-san of Kyōng-syang Do, and the opposite the Chyōlla Do Chiri-san. The axial ridge turns its fault-scarp to the east. If we compare this with the Median ridge of the Thai-Päik-san, the Hoang-chhi ridge should be placed parallel with the coastal ridge. Through the undulating hilly land goes a road from San-chhyōng to Chi-ryōi<sup>7)</sup> through An-eui<sup>8)</sup> and Kō-chhyang. It is remarkable to find that this comparatively easy, intermontane highway is not recognized by any except by the natives. It goes along the foot of the inner ridge parallel to the course of the middle Nak-tong Gang, though we have to cross several hill necks of naked, decomposing granitic rocks.

iii. *The Yuk-sim-nyōng Ridge*.—Again the ridge starts from the headland of Heung-yang<sup>9)</sup>, and passing the passes of Pul-chhi<sup>10)</sup> (320 m.) and Chyōn-san<sup>11)</sup> of Nak-an<sup>12)</sup>, Pam-chhi<sup>13)</sup> and Yō-uōn-chhi<sup>14)</sup> (435 me-

1) 黃石山(東門山)

4) 雙溪寺.

7) 知禮.

10) 火峙.

13) 栗峙.

2) 巨昌.

5) 九月山

8) 安威.

11) 金錢山

14) 女院峙

3) 德大山.

6) 妙香山 or 香山

9) 興陽.

12) 樂安.

ters) of Nam-uön<sup>1)</sup>, Yuk-sim-nyöng<sup>2)</sup> (690 m.), Tög-yu-san<sup>3)</sup> and then Pu-hang-nyöng<sup>4)</sup>, it finally comes to end at Chik-chi-san<sup>5)</sup> near the Chhyu-phung-nyöng pass. In its northern prolongation it forms the boundary ridge of two provinces, and Tög-yu-san, its highest point, is frequently mentioned by native geographers. The steep side of the ridge by this time lies on the west in contrast to the two preceding ridges; consequently this together with the axial ridge forms a sort of crust-block or *Horst*, similar in structure to the Thai-Päik-san. A narrow table of Un-bong<sup>6)</sup>, 370 m. high, lies between the ascents of Yö-uön-chhi (west) and Phal-hyöng-chhi (east side).

iv. *The Pi-hong-chhi Ridge*.—This westernmost member starts from the head-land of Thyön-goan-san<sup>7)</sup>, and advances by Să-chă-san<sup>8)</sup> Kamnamu-chhi<sup>9)</sup> (150 m.), Tong-pok<sup>10)</sup>, the Pi-hong-chhi pass<sup>11)</sup> (215 m.) of Nam-uön, the Pha-kokăi<sup>12)</sup> (310 m.) of Chin-an<sup>13)</sup>, ending at the same point as the preceding.

The ridge is like in structure to its eastern neighbour, and between them is situated the depression of Nam-uön.

The foregoing four members, as has been already stated, converge to the Chhyu-phung-nyöng pass where the apex of the gigantic Chiri-san wedge lowers to 200 meters, and the said pass affords an easy passage from the north to the south. The point is just midway of the projected Fusan-Seoul Railway. To the *feather-structure* of these ridges, I shall come back in later pages.

### c. THE HAN-SAN RANGE.

Putting aside the Kai-ma Land as an exception, Korea is not a

- |        |         |        |
|--------|---------|--------|
| 1) 南原  | 2) 六十嶺  | 3) 德裕山 |
| 4) 釜項嶺 | 5) 直指山  | 6) 雲峰  |
| 7) 天冠山 | 8) 獅子山  | 9) 柿峙  |
| 10) 同福 | 11) 飛鴻峙 | 12) 波峙 |
| 鎮安 13) |         |        |



very high mountainous country, nevertheless we find mountains every where. It is topographically speaking a labyrinth, and one will find orientation very difficult in the country without the help of good maps. The general disposition of the land is like a checker-board; this being due to the crossing of mountain-directions. *I have already enumerated about 10 ridges of the Korean System, all running more or less north-south, terminating in head-lands, peninsulas and islands in the Southern Archipelago.* As instances of these southerly projecting points may be mentioned Ta-thai-pho near the mouth of the Nak-tong Gang, Kō-chyōi and Nam-hăi Is., the peninsulas of Yō-syu and Heung-yang, the head-lands of Thyōn-goan-san and Tai-dun-san<sup>1)</sup>, and lastly, the island of Chin-to<sup>2)</sup> at the south-west corner of Korea. The last-named island marks the boundary of the Southern and Western Archipelagoes, and divides the waters of the Yellow Sea from those of the Nam-hăi or South Sea.

Any one, coasting round the archipelago, will readily notice where the *Yellow Sea begins by its turbidity and yellow colour.* This peculiarity arises apparently from complicated causes. Swift currents, shallowness of the waters near the coast and great differences in tidal height\* are the principal factors which stir up the water and make it muddy.

1) 大屯山.			2) 珍島		
* Spring-tide. Neap.			Spring-tide. Neap.		
West coast.	Mouth of the Tai-dong Gang	21½ ft. 15½ ft.	South coast.	Chyang-ching-no harbour	11½ ft. 7½ ft.
	Chyang-san-kot	14 10½		Teung-nyang Bay	13½ 8½
	Mouth of the Han Gang	34 —		Port Hamilton	11 —
	Che-mul-pho	29½ 24½		Yō-chū Bay	13½ 8½
	Su-chhyōk Group	16 10½		Yō-syu Bay	12½ 7½
	Na-jyu Group	13 9½		Tha-ryang Ferry (Sea of Han-san-to)	10 6½
	Great Heuk-san-to Group	10½ 4		Kō-chyōi Is. (east coast)	6½ 4½
	Mok-pho	14 10	East coast.	Fusan	7 —
	Chin-to Is.	14½ 9½		Gen-san	1½ —
				Syō-syu-ra Anch	3 4 —
				(Tuman Gang)	
Maru Gulf					
		15 9½			
So-an-do Group					
		10½ 7½			

Corresponding to these *outcurves* of coast-lines, we have numberless *cores*, *inlets* and *bays*, the principal of which, counting from the east, are the following :—The twin bays of Chin-hăi and Ma-san-pho, north of the Kō-chyōi Is., the Sea of Han-san-to, the Bay of Yō-syu receiving the water of the Syöm-jin Gang, the incurves of Yō-chă<sup>1)</sup> and Teung-nyang<sup>2)</sup> on the east and west sides of the Heung-yang peninsula, the harbour of Chyang-ching-no<sup>3)</sup>, and lastly, the Gulf of Ma-ru<sup>4)</sup> or Washington. So numerous are the islands and islets here that I can scarcely enumerate them.

*The complexity of the southern coast is the joint-result of the mountain-building of the Korean and the Han-san Systems ; of the latter I shall now speak somewhat in details.*

Broadly speaking, the *System* stretches E. N. E., sometimes due east, and even bends a little to the south. There seems to exist a great number of ridges, all being the edges of dislocation, in South Korea. The earth-movement here took place on a less grand scale than in the case of the two preceding systems, so as to give a pronounced effect on land-physiognomy. I will select a few principal instances.

i. *The Pam-chhi Ridge*.—This is a somewhat irregular ridge starting from the north of Koang-jyu, and crossing the upper Syöm-jin Gang near Kok-syōng. The Pam-chhi pass between Nam-uön and Ku-ryōi<sup>5)</sup> is its typical scarp facing the Nam-uön depression of erosion (50 m). It then pursues a north-easterly course to the south of the Phal-hyōng-chhi pass and Ham-yang, whence it can be traced as far as Koan-bin. A new scarp begins at the south of Ham-yang, trending south-eastwards cutting Chiri-san on the north; and San-chhyōng is situated at its north foot, hence the place was formerly called San-eum or the Moun-

1) 汝自灣

2) 得根灣

3) 長直路 or Sin-ji-do (薪知島)

4) 馬路

5) 求禮

tain-shadow. A river flows through a gorge of the ridge near that place toward Chin-jyu. Chiri-san viewed from the north is majestic.

ii. *The Neung-jyu Ridge*.—From the Na-jyu plain we see on the south toward Neung-jyu<sup>1)</sup> a ridge running eastwards from the celebrated Uöl-chhyul-san<sup>2)</sup> of Yöng-am<sup>3)</sup> with a precipice facing us like the preceding. For a while it is lost in the hilly land of Tong-pok<sup>4)</sup>, reappearing near the Chan-syn<sup>5)</sup> ferry of Ku-ryöi. It then crosses the Syöm-jin Gang at the north of Ha-dong, and proceeds north of the Hoang-chhi toward the south of Chin-jyu and Chin-häi. The *middle Syöm-jin Gang is deflected to an easterly course by this ridge*. The road goes along its northern foot between Chin-häi and Chin-jyu in Kyöng-syang Do, and between Ku-ryöi and Na-jyu viâ Tong-pok.

iii. *The Pyöng-yöng Ridge*<sup>6)</sup>.—This begins at Häi-nam and goes along the north of Kang-jin<sup>7)</sup>, Chyang-heung<sup>8)</sup>, Po-syöng<sup>9)</sup>, Nak-an<sup>10)</sup> and Syun-thyön<sup>11)</sup> (Sol-chhi<sup>12)</sup>, 240 m.), Koang-yang<sup>13)</sup> as far as Ko-syöng<sup>14)</sup>, after traversing the Syöm-jin Gang and the Să-chhyön<sup>15)</sup> inlet. The fault scarp by this time faces *south*, and though it is not a high one, it marks the water-parting on the south-coast. A tolerably *fair road* is constructed between Syun-thyön and Häi-nam along the south foot of the ridge.

Still *other ridges of similar structure and parallel orientation* are seen, one along the coast and the other through the Chyang-ching-no islands<sup>16)</sup>, Heung-yang, Yö-syu, the islands of Nam-häi and Kō-chyöi.

1) 綾州.

2) 月出山.

3) 靈岩.

4) 同福.

5) 潺水.

6) 兵營.

7) 康津.

8) 長興.

9) 寶城.

10) 樂安.

11) 順天.

12) 松峙.

13) 光陽.

14) 固城.

15) 泗川.

16) 長直路 or Sin-ji-do.

In Kyöng-syang Do, I could trace many ridges of this system, sometimes dislodged towards the south, sometimes toward the opposite side. *One* of these runs north of Chin-hăi<sup>1)</sup> and Ung-chhyön, after passing over the narrow inlet of Ma-san-pho, with its precipitous wall towards south. The *second* ridge trends eastwards between Chhil-uön<sup>2)</sup> and Chhyang-uön<sup>3)</sup>, and then to the north of Kim-hăi<sup>4)</sup>. It crosses the Nak-tong Gang at the fortified gorge of Kkachhi-uön-koan<sup>5)</sup>, ending at the sea near Keui-jyang<sup>6)</sup>. Its steep side is on the north, and to it is entirely due the *remarkable angle of the Nak-tong Gang at Yöng-san*<sup>7)</sup>. The *third* lies on the north of the angle between Mil-yang<sup>8)</sup> and Chhyöng-do<sup>9)</sup>, and passes through the Un-mun-nyöng<sup>10)</sup>, and then Mal-li-syöng<sup>11)</sup> between Ul-san and Kyöng-jyu. The *fourth* stretches to the north of the town Tai-ku at the granitic mountain of Phal-kong-san<sup>12)</sup>. I have still to mention the Mo-chă-san<sup>13)</sup> ridge in the plateau (300 m.) of Yöng-chhyön.

I have grouped together all these fault-scarps and ridges under the Han-san Range, by which the peninsular block has been successively dislodged southward, thus limiting the south border of Korea. Small peninsulas, head-lands, islands, islets and rocks are only the detached masses and fragments with skeletal ridges of the Thai-Păik-san and Han-san ranges. Hundreds of these fragments abound in the South Korean Archipelago.

The Han-san Range is *younger* than the two preceding, *viz.*, the

- 
- 1) 鎮海  
4) 金海  
7) 靈山  
10) 雲門嶺  
13) 母子山

- 2) 漆原  
5) 鵲院關  
8) 密陽  
11) 萬里城

- 3) 昌原  
6) 機張  
9) 清道  
12) 八公山

Sinian and the Korean, and moreover, I believe it is the *youngest* of all the mountain-ranges met with in the whole of Korea.

*What the real position of this system is in relation to those prevailing in Japan and China, I am not able to tell.* The western half of Hondo (Japan) seems to have been greatly influenced by this system. In the interior of South China it seems to have some connection with the low series of mountains which decides the *lower course* of the Long River. These low ranges are probably members neither of the Kuen-lun, nor the Sinian. We lack a detailed knowledge of these low *basin-ranges* of the Yang-tze-Kiang.

## B. THE KAI-MA LAND.

North Korea, as I have already stated, is divisible into two regions, *viz.*, the plateau of Kai-ma on the north, and the hilly land of Paleo-Chyo-syön on the south. The boundary between the two is sharply marked. The north is a *high plateau* with a fault-scarp, facing southwards towards the depressed land, just as the Great Khingan (Hsing-an) turns to the east with its precipice towards Manchuria. The incurves of Korea Bay on the west and that of Chyo-syön Bay (Broughton Bay) on the opposite side give some idea of the boundary as expressed in coast-lines, and we can trace it in the interior as well.

The *natural limit is so distinctly marked* that in 1033, Tök-chong<sup>1)</sup>, the ninth king of Ko-ryö, ordered his subject Yu-syo<sup>2)</sup> to build a stone-wall, 25 feet high and thick, across the peninsula so as to check the incursions of *Nüchens*<sup>3)</sup> and *Chitans*<sup>4)</sup> from the Manchurian

1) 徳宗.

3) 女眞.

2) 柳詔之長城 ("the Great Wall of Yu-syo").

4) 契丹.

frontier, perhaps after the model of the *Great Wall* of China, constructed B.C. 220 by Shi-hwang-ti<sup>1)</sup> of the Tsin<sup>2)</sup> dynasty to ward off the inroads of *Huing-nu*<sup>3)</sup> from Inner Mongolia. It is stated<sup>4)</sup> that the so-called Wall of Yu-syo begins at Yong-man<sup>5)</sup> at the mouth of the Am-nok Gang and crosses through Wi-jyu<sup>6)</sup>, Un-san<sup>7)</sup>, Heui-chhyön<sup>8)</sup>, Yöng-uön<sup>9)</sup>, Mäing-san<sup>10)</sup>, Yo-dök<sup>11)</sup> of Yöng-heung<sup>12)</sup>, finally reaching the Sea of Japan at In-pho<sup>13)</sup> in the Ham-heung<sup>14)</sup> district.

During my journey I saw no continuous wall which might be looked upon as the ruin of this fabulous engineering-work; but I frequently passed strong stone-gates at strategically important points, such as at the foot, and on the passes of mountains. On the highway to China I have passed the double-roofed gates of Syö-rim-chin<sup>15)</sup> and Tong-nim-chin<sup>16)</sup> on the south of Wijyu, on the passes of Ö-jä-ryöng<sup>17)</sup>, and Chhya-ryöng<sup>18)</sup> in Un-san, and Työk-yu-ryöng<sup>19)</sup> in Heui-chhyön,—all in North Phyöng-an Do. Likewise there are many such in North Ham-gyöng Do. The Koreans seem to have availed themselves of the natural defence of the mountain-ridges, and to have fortified only the most important points. The Koreans were and are still very nervous because of their past sufferings. They have to fear enemies from both north and south. From the latter they have to guard against the encroachments of the Japanese. Travellers will see the towns fortified from Kang-uön Do all along the south coast,

1) 始皇帝.

2) 秦.

3) 匈奴.

4) in *Ko-ryö-sü* (高麗史).

5) 龍灣 (a name given to the mouth of the Am-nok river or Ya-lu-kiang).

6) 義州.

7) 雲山.

8) 熙川.

9) 寧遠.

10) 孟山.

11) 耀德.

12) 永興.

13) 麟浦.

14) 咸興.

15) 西林鎮.

16) 東林鎮.

17) 於自嶺.

18) 車嶺.

19) 狄踰嶺.

and in these intermural hermit-towns the people seek in vain a peaceful life.

### a. THE LIAU-TUNG RANGE.

The earth-movements that disturbed and uplifted the Kai-ma Land are mainly dislocations and not folds ; consequently the disturbance should be classed in the same category as that which created the Korean and the Han-san systems. *I can without difficulty distinguish three ridges, which run parallel to one another in the Liau-tung direction and constitute the skeleton of this northern plateau.* The two southernmost of these have the steep side towards the south, but it is remarkable that they become successively higher at the tilted edge, when the block is suddenly cut off to a lower level on the south. The tilted edge of this narrow but gigantic block is, as I have already stated, the land-mark of the two halves of North Korea. The third parallel ridge, however, falls away steeply to the north-west : in consequence of which a comparatively low basin is formed in the drainage-area of the Am-nok and the Tuman rivers, which is limited on the north by the long Chyang-päik-san.

i. *The Myo-hyang-san Ridge.*—We can trace this ridge from Kōm-san<sup>1)</sup> in Korea Bay on the north of Syōn-chhyōn<sup>2)</sup> towards the east through Thai-chhyōn,<sup>3)</sup> and Yōng-byōn<sup>4)</sup> across the Upper Chhyōng-chhyōn Gang<sup>5)</sup> in Uōl-lim<sup>6)</sup> at the entrance of the famous Myo-hyang-san<sup>7)</sup> until it culminates at Koang-syōng-kokāi<sup>8)</sup>. The ridge within Phyōng-an Do is of moderate height, though presenting a sharp outline : but after entering Ham-gyōng Do it assumes an imposing appearance, marking the south brink of the Eastern Kai-ma plateau.

1) 劍山.

2) 宣川.

3) 秦川.

4) 寧邊.

5) 清川江.

6) 月林, hence the upper course of the river is named the Uōl-lim Gang.

7) 妙香山 or Hyang-san

8) 廣城峴

On the way from Ham-heung to Chyang-jin<sup>1)</sup>, I made the ascent of one of the passes of this ridge called the pass of Hoang-chho-ryöng<sup>2)</sup> (1090 m.). I literally climbed up to the summit on a narrow, rocky path running through a deep forest, and one of my loaded ponies lost his foot-hold and fell twice throwing off his load. Midway up we had to make a short descent at which time my horse-drivers caught the ponies by the tail to prevent them from slipping.

The ridge then runs eastwards through Pu-chyöl-lyöng<sup>3)</sup> and Hu-chhi-ryöng<sup>4)</sup>, being finally cut down by an oblique fault-line at *Tai-uön-san-nyöng* (1375m)<sup>5)</sup>. The latter, starting from near the free port of Syöng-jin<sup>6)</sup>, proceeds northwards along the coast, penetrating far into the Tuman Gang region, and the northerly curve of this boundary river follows its eastern foot. The new ridge is popularly known as the Chyang-päik-san, but it should rather be called the Small or *Syo-Chyang-päik-san* to discriminate it from the Long-white Mountains of the north. The ridge is the eastern brink of the basalt-plateau of East Kai-ma, and the coast of Ham-gyöng Do from Syöng-jin to Kyöng-syöng follows the course of the mountain, exactly like the Kang-uön Do coast at the foot of the Thai-Päik-san-range. The Myo-hyang-san, after being cut off from the main ridge by the Syo-Chyang-päik-san, still lingers near the coast, keeping its original direction, and raising its head of *geological cliff* within basalt-mesa. It is locally called Kang-neung-san<sup>7)</sup>, and ends at Ö-tai-jin-kot<sup>8)</sup> (C. Kozakoff).

The foreland between Syöng-jin and Ham-heung borders the north shores of Chyo-syön Bay. It is a belt of hilly land about 40 kilometers in width, with the precipitous wall (1000 m.) of the Myo-hyang-san on the north. This tract was called in the middle ages

1) 長津

4) 厚致嶺

7) 江陵山

2) 黃草嶺

5) 大元山嶺

8) 漁大串

3) 赴戰嶺

6) 城津



Kal-lan<sup>1)</sup>, and the high *hinterland* the Sol-bin<sup>2)</sup> Land, the latter approximately coinciding with the often-mentioned East Kai-ma. The only highway to Vladivostok runs along the coast where one must cross the Ham-koal-lyöng<sup>3)</sup>, Ma-ul-lyöng<sup>4)</sup>, and Ma-thyöl-lyöng<sup>5)</sup> between Ham-heung and Syöng-jin. These *three passes* are on independent ridges which go through East Kai-ma, and probably also through the Upper Sungari in the Trans-Chyang-päik Mountains. *Their directions approximately coincide with the general trend of the Thai-Päik-san ; but I believe their upheaval dates far back in time as compared with the mountains of South Korea.*

ii. *The Työk-yu-ryöng Ridge.*—Starting at about the same point as the preceding with similar geologic structure and approximately in parallel orientation, this ridge passes through Yong-kol-san<sup>6)</sup> and Syö-rim-chin<sup>7)</sup> (100m.), the above-mentioned O-jä-ryöng (510m.) and Chhya-ryöng (635m.) near the American mines of Un-san, then through Ku-hyön<sup>8)</sup> and Työk-yu-ryöng<sup>9)</sup> (970m.); the last lies on the main road from the southern Phyöng-an Do to Kang-gyöi<sup>10)</sup> which is the center of commerce and the headquarters of troops, of the middle Am-nok Gang. Kang-gyöi is comparatively speaking a busy town and claims an important commercial position in northern Ham-gyöng Do, as Hoi-ryöng<sup>11)</sup> does for the upper Tu-man Gang. In East Kai-ma Land the ridge forms Yün-hoa-san<sup>12)</sup> and Syöl-mäi-ryöng<sup>13)</sup> (1,400m.) of Chyang-jin<sup>14)</sup>, apparently becoming lower towards the Sam-syn<sup>15)</sup> district.

1) 曷羅

2) 率濱

3) 咸關嶺

4) 摩雲嶺

5) 摩天嶺

6) 龍骨山

7) 西林鎮

8) 狗峴

9) 狄踰嶺

10) 江界

11) 會亭

12) 蓮花山

13) 雪庵嶺

14) 長津

15) 三水, or Three Waters, so named as it lies in the region at the junction of the Am-nok, Hô-chhyön and Chyang-jin rivers.

I do not know its eastern prolongation as it is hidden in the impenetrable forest of basalt-mesa on the upper course of the Tu-man Gang. We see in the hilly land of Yuk-chin<sup>1)</sup> a ridge running north-eastwards from Pu-ryöng to Ung-geui-pho<sup>2)</sup> (Audacious Cove). This is the *Chhyöng-baho*<sup>3)</sup> ridge, and may be looked upon as a continuation of the long Työk-yu-ryöng Ridge.

iii. *The Kal-eung-nyöng Ridge*.—The third and the last ridge of the Liau-tung direction in the Kai-ma Land bounds the hydrographic basin of the Am-nok and Tu-man rivers on the south, from which the uplifted block descends slowly in the undulating folds of gneiss. The ridge can not be recognized as such from the plateau, but is easily seen from the basin-region.

The ridge proceeds from Ok-gang<sup>4)</sup> on the Am-nok Gang through Mang-nyöng<sup>5)</sup>, Oan-hang-nyöng<sup>6)</sup> (640m.) of Chhyang-syöng<sup>7)</sup>, Sam-chhăi-ryöng<sup>8)</sup> (810m.) of Chho-san<sup>9)</sup>, and passes over the gorge of Syang-chhyöng<sup>10)</sup> on the south of Kang-gyöi. Then it touches the pass of A-deung-nyöng<sup>11)</sup> between Kang-gyöi and Chyang-jin, and continues to Kal-eung-nyöng<sup>12)</sup>, crossing the upper Am-nok river at

1) The low mountainous tract at the north-east corner of Ham-gyöng Do, partially enclosed by the outcurve of the Tu-man Gang, is popularly called Yuk-chin (六鎮地方). The region was the source of troubles under the Ku-ryö dynasty. The *Orangkhalis* (兀良哈) or *Yö-chin* (Nüchen 女真) barbarians often made inroads into this side of the Tu-man Gang from their home, lying between Chyang-päik-san and Hei-lung Kiang (the Amur), sometimes incorporating Ham-gyöng Do in their own domain. Syöi-song, the fourth King (1418-1449) of the present dynasty, recovered all that had been lost and established six military stations or *chins* along the great curve of the Tu-man Gang. They are Kyöng-heung (慶興), Kyöng-nön (慶源), On-syöng (穩城), Chyong-syöng (鏡城), Hoi-ryöng (會寧) and Pu-ryöng (富寧). At a later time Mu-san (茂山) was added to them. Hence the region within the outcurve of the river and Kyöng-syöng (鏡城) is designated *Yuk-chin* or Six Military Stations. At remote times it went under the name of Măi-ku-rn (賈溝婁).

2) 雄基浦.

3) 青岩 or blue rock is a vertical reef, running across the river-bed, 5 kilometers south of Pu-ryöng. It is a dyke-rock in gneiss-granite oriented in the same direction as the trend of the ridge. The rock is a red, compact quartz-porphry and not a blue one.

4) 玉江.

5) 幕嶺.

6) 緩項嶺.

7) 昌城.

8) 三絲嶺.

9) 楚山.

10) 尙清.

11) 牙得嶺.

12) 聖靈嶺.

Chhyung-thyöl-lyöng<sup>1)</sup>, where the Duck's Green river makes a deep gorge. In its further course I know nothing about it, though the already-mentioned *Chhyong-bahoi ridge* in Yuk-chin indicates some connection with it in regard to the orientation of mountains.

At the north-east corner of Ham-gyöng Do, in the so-called Yuk-chin district which comes in direct contact with the Russian Littoral territory, is a ridge which I have already mentioned—the Chhyöng-bahoi. There are still two others worthy of mention which I recognized during my journey there.

a) One sharp ridge—the *Mu-san-nyöng*<sup>2)</sup> with south scarp comes from the famous Päk-tu-san in almost equatorial direction through Mu-san, and the Mu-san-nyöng pass; the latter lies between Hoi-ryöng and Pu-ryöng. In its further course it goes through Chyönn-nyöng<sup>3)</sup> and just before Kyöng-heung crosses the Tu-man Gang to the east at the boundary of Manchuria and Primorsk.

b) The other ridge—the *Chyang-ji-bong*,<sup>4)</sup> of the same geologic structure, runs on the north side of the Tu-man Gang in the neutral district of Kan-to,<sup>5)</sup> and crosses the meridional course of the river at the north of Hoi-ryöng, culminating at Chyang-ji-bong near Hang-

1) 衡天嶺

2) 茂山嶺

3) 楡嶺

4) 長支峰

5) We were accustomed till a few years ago to see on the maps of China a long belt of neutral territory on the west of the Am-nok Gang, and the Korean Gate in the palisade near Föng-hwang-tchön marked the true eastern limit of South Manchuria. At present this territory is *in actu* absorbed by China and has disappeared forever from the map. The Duck's Green river forms now the international boundary. This side is inhabited by the white-clothed Koreans, the opposite side by the blue-clothed Chinese.

We have still a relic of such a territory in the region of the ten-thousand waters. Near On-syöng one finds a great tributary river joining the Tu-man Gang. This rises in Päk-tu-san, and in its course receives the name Hái-ran-ha (海蘭河) or the Boundary river. On its north side is the high basaltic plateau of Kirin. The basalt-mesa lying between this river and the Tu-man Gang embraces an extensive area, 120 kilometers long and 60 kilometers wide, and equals in size that of Yuk-chin. This region is called the *Interrening Island* or *Kan-to*, and in former times it was entirely without inhabitants and was kept strictly as a neutral territory. Lately, however, under the pressure of the Russian advance toward the south the Chinese and the Koreans have settled there and are living together; so trouble often arises between the two countries as to the government of its inhabitants.

yöng, the headquarters of Yuk-chin. It then crosses again the river at the north of Kyöng-heung, apparently ending on the south side of Possiet Bay in the Russian dominion. A Russian military station, Savlofka, lies at the foot of the ridge on the north side of the river just opposite Kyöng-heung.

The road from Kyöng-heung to Hoi-ryöng across Yuk-chin goes between the two ridges, and the course of the Tu-man Gang is for a short distance deflected on the south foot of this ridge, corresponding to both arms of the U-shaped outcurve of the Tu-man Gang.<sup>1)</sup>

A glance at the structural lines of the north border of the peninsula, will lead one to conclude that the above-mentioned ridges converge or rather approach each other near the mouth of the Tu-man Gang. Ranges of the Kai-ma Land trend E.N.E., while those of Yuk-chin run nearly due east. I here wish to call particular attention to the fact that the latter are in the *Chyang-päik-san direction* in contrast to that of the Liau-tung.

F. v. RICHTHOFEN's geologic map of Liau-tung shows structural lines analogous to those of my field, and both form, indeed, a geologic unit. Moreover, a recent journey of E. v. CHOLNOKY<sup>2)</sup> disclosed another ridge with the E. W. trend near San-tao-kou, which, I believe, lies further north of the Chyang-päik-san, apparently with the same structure as in my field. He says that the geologic line cuts through Tung-hoa-hsien and reappears near Tieh-ling<sup>3)</sup> in the complex of phyl-

1) *Tu-man* or *to-man* signifies ten-thousand in the Nüchen dialect; Tu-man Gang, therefore, means ten-thousand waters or a stream having innumerable tributaries. I believe the name originated from the feather-like arrangement of its affluents which flow down from the basalt-mesa of Kai-ma in the upper course of the stream.

2) 'Kurze Zusammenfassung der wissenschaftlichen Ergebnisse meiner Reise in China und in den Manchurei in den Jahren 1896-1898.' *Verhandlungen der Gesellschaft für Erdkunde zu Berlin.* Bd. XXVI. 1899, S. 255.

3) 鐵嶺.

lite, gneiss and gneiss-granite with a northerly dip. The same ridge seems to continue to the other side of the Liau-tung depression at I-wu-li-shan. This had been asserted a century before by a Korean geographer<sup>1)</sup> whose statement is now reaffirmed by Dr. E. v. CHOLSKY. It seems to me that the further north we go, the younger is the geological event which lifted up the block on the south edge with northerly slant.

The Am-nok-Tu-man Gang basin is in one of these valleys of *compound step-fault*,<sup>2)</sup> which is at the same time one of the widest. Had not the lava from the Păik-tu-san volcano, the highest point of the Chyang-păik-san, flowed down to the south, and partially filled up the bottom, we should have a comparatively low trench through which an easy path might lead from Possiet Bay to the Angle of Mao-êrh-shan in the upper Am-nok. An elevation which separates the two rivers is the pass of Hyöi-san-nyöng<sup>3)</sup> whose altitude possibly does not exceed 700 meters. During the Augustine age of the Liau<sup>4)</sup> dynasty (916-1125) their sovereigns yearly sent an expedition through this valley to get falcons from the Lower Tu-man. Hence the way through the two rivers was called the *Falcon road* or *Fung-no*.<sup>5)</sup> It is now entirely forgotten, and, as we see now, the upper Tu-man is a pathless, impenetrable forest. It was not Nature, but man who drove civilization out of this region, and the fact that the region lies near the sacred home of the Manchu dynasties, has greatly contributed to this condition of abnormal retrogression.

1) I-Chyung-hoan. *Vide ante* p. 6.

2) Exactly speaking, the present case is what the miners call the *hading against the dip*, and the parallel fault planes are all inclining in the same sense.

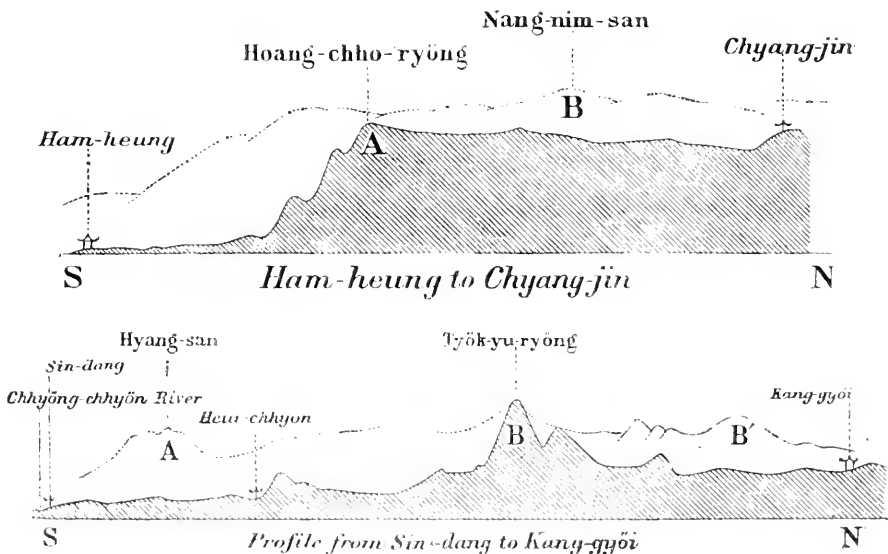
3) 惠山嶺

4) Liau or Kitans or Cathay (遼)

5) 鷹路.

## b. THE KOREAN SYSTEM.

When speaking of the surface-configuration of South Korea, I have said that it is like a checker-board, and the same feature is not wanting in the Kai-ma Land. We have here mainly to deal with the Thai-Päik-san Range. The Kai-ma Land is naturally divisible into two portions. The right side is East Kai-ma or the Sol-bin Land which presents the typical physiognomy of a plateau, especially the part lying between the Hyang-san and Työk-yu-ryöng ridges, with an average-height of 1,000 to 1,200 meters. (Fig. 3.) The water-divide lies in the first ridge. The left side is less typical, on average 600 meters high, and the Työk-yu-ryöng ridge is here the water-parting. (Fig. 4.)



Scale 1:562,500. Vertical  $\times 2$ .

Fig. 3.—Profile from Ham-heung, the general magisterial town of South Ham-gyöng Do, to Chyang-jin through the pass of Hoang-chho-ryöng (1090 m.), showing the typical plateau-feature of the East Kai-ma land. A and B are the Hyang-san and the Työk-yu-ryöng ridges. The Kal-ong-nyöng ridge lies to the north of Chyang-jin.

Fig. 4.—The profile is drawn from Sin-dang, 50 kilometers up the river Chhyöng-chhyön from An-ju, to the inland town of Kang-gyöi through the celebrated Mount Hyang-san and the Työk-yu-ryöng pass. (970 m.) This cross-section shows the much-dissected plateau of West Kai-ma. A, B, and B' are respectively the Hyang-san, Työk-yu-ryöng, and Kal-ong-nyöng ridges.

i. *The Nang-nim Ridge.*—An important ridge which separates both Kai-mas, seems to me to be a continuation of the Thai-Päik-san of South Korea. It is the Nang-nim-san<sup>1)</sup> ridge with the escarpment toward the west. Nang-nim-san itself, as far I could make out, seems to be a branch of the Työk-yu-ryöng ridge. The Tai-gang-syöm<sup>2)</sup> peninsula at the entrance of Yöng-heung Bay bridges over Nang-nim with the Keum-gang-san portion of the Thai-Päik-san range. It encloses landwards the inlet of Syong-djyön<sup>3)</sup> or Port Lazareff. Its northern prolongation is not well ascertained, but as FREIHERR FERDINAND VON RICHTHOFEN suggests<sup>4)</sup>, the angle of Mao-êrh-shan,—the sudden turn of the river-course of the Am-nok,—must be ascribed to its presence. Its further course may perhaps be traced in the geologic structure though it may not be apparent in surface-features.

ii. *The Ham-koal-lyöng Ridge.*—In East Kai-ma I have still to mention two other ridges which lie to the east of the preceding and run approximately in the same direction, but with the fallen blocks on the contrary side, consequently presenting sharp scarps toward the east. In both trend and structure, they must be grouped with the Thai-Päik-san range.

The Ham-koal-lyöng ridge, as has been already stated, starts from the gneiss pass of the same name between Ham-heung and Hong-uön<sup>5)</sup>. I have crossed it in the eye-gneiss region of Syöl-lyöng (1,565 m.) in the interior. Perhaps in its farther course it meets the Kal-eung-nyöng ridge at the gorge of Chhyung-thyöl-lyöng in the Am-nok Gang.

iii. *The Ma-thyöl-lyöng<sup>6)</sup> Ridge.*—The pass of the same name (600 m.) lies to the west of the free port of Syöng-jin. It is a well-

1) 狼林.

2) 大江島半島 or Nakhimof Peninsula

3) 松田灣.

4) *Vide ante* p. 5.

5) 洪原.

6) 摩天嶺.

known land-mark which separates the north Ham-gyöng Do from the south. This and the other side are respectively called Nam-koan<sup>1)</sup> and Peuk-koan<sup>2)</sup>, *i.e.* the south and the north of the gate. I have met with it on the way from Kap-san<sup>3)</sup> to Kil-jyu<sup>4)</sup>, in the form of gneiss (the axis of schistosity N. 30° W., and vertical) in the celebrated gold field in the canyon-like Tai-dong<sup>5)</sup> valley of Tan-chhyön<sup>6)</sup>. A geologic cliff by the name of Tu-ryu-san<sup>7)</sup>, 2,421 meters high, raising its head from the basalt-mesa, points out the direction in which the ridge runs in the high, lava-drowned flat<sup>8)</sup>.

As above stated, I have no local knowledge of the upper Tuman Gang; yet if the line be traced northwards, it would touch the water-divide of Hyöi-san-nyöng and finally reach the volcano of Păik-tu-san. *Should my supposition prove to be right, then the crater would be located at the intersection of the two tectonic lines.*

The *three ridges*, which I have just treated in general outline, have the trend in the Thai-Păik-san direction, yet their peculiar characteristics prevent them from being classed together in the same group. Starting from the magisterial town of Ham-heung, north of Wön-san, toward the pass of Hoang-chho-ryöng, we find ourselves walking upon the ground of a whitish, coarse, *crushed granite* whose schistose axis runs at first in the Sinian direction<sup>9)</sup> (S.W.—N.E.) till the foot of the pass is reached. Then the axis suddenly changes: to the Liao-tung direction on the pass. From here to Chyang-jin for a two day's march the *pressed axis of the rock is oriented north-south with westerly trend within a few degrees* (less than 20°), which coincides with that of the Thai-Păik-san.

1) 南關.

2) 北關.

3) 甲山.

4) 吉州.

5) 大洞 See Pl. II, Fig. 2.

6) 端川.

7) 斗流山

8) See Pl. II, Fig. 1.

9) It is the Măing-jyu-nyöng Ridge.



I believe this is the primary structure, as is evinced from extended, black secretionary patches and also excretionary, coarse, tourmaline-bearing aplite. May not this structure have been caused by the active flow of soft rock after the fashion of an ice-sheet, or by a passive movement during the folding of the crust? The two ridges,—the Ham-koal-lyöng and the Ma-thyöl-lyöng,—are no doubt crests of the pressed granite. Between Kap-san and Kil-jyu the compressed rock is overlaid discordantly by phyllite and limestones which are in turn covered by flat basalt-flows<sup>1)</sup>. From the mode of occurrence of the fundamental rock I am forced to conclude that the crustal movement took place in a very old period, and therefore that it has lost its topographic significance. These ridges should have their prolongation in the Sea of Japan, unless they be cut down to the abyssal bottom by the later Liao-tung ridges.

The meaning of these ridges and of the pressed planes of gneiss-granite in East Kaima is not clear to my mind ; and the difficulty of deciphering their import becomes to me a constant stumbling block in my attempts at reconstructing the geological history of the peninsula.

*The geologic axis of the gneiss-granite coincides with that of the Korean system, but it may not be identical with the axis which prevails in the Thai-Päik-san range.* F. von RICHTHOFEN<sup>2)</sup> repeatedly speaks of an old geologic line in Shan-tung, running N.N.W. to S.S.E., and this seems to have something to do with that which I have observed in East Kai-ma. It may perhaps represent the fourth line of W. Prinz's torsion-course<sup>3)</sup>.

It must be specially remarked that this highly significant line of geologic structure was not noticed in West Kai-ma, excepting in a

1) See Pl. II, Fig. 1.

2) 'Schantung', S. 53

3) *Annuaire de l'Observatoire Royal de Bruxelles*, 1891

spot at Chhya-ryöng on the north of the American Mines of Un-san. The said structure seems to prevail mainly to the east of the compound ridge of Thai-Päik-san and Nang-nim, which together form the present back-bone of the Korean Peninsula.

There are *three ridges* of the Thai-Päik-san range in West Kai-ma. As they are inseparable from those in the land of Paleo-Chyo-syön, it will be convenient to treat them in the sequel.

### C. THE PALEO-CHYO-SYÖN LAND.

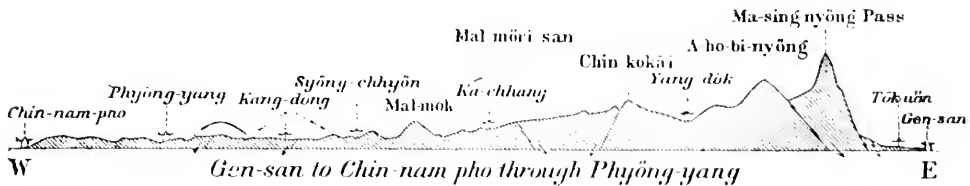
Between the axes of mountains of the Sinian and Liao-tung directions which seem to join in East Kai-ma and Yuk-chin, there is present a wedge-shaped tract of land *inserted* between them, which remained in a neutral state, or rather took a retrogressive movement to the south-west between the two struggling forces. Geologically speaking, it is a folded Sinian land. Lying to the north-west of the trench of Chyuk-ka-ryöng, which separates South from North Korea, this *Intersertal* makes up the southern half of the latter, being bounded on the north by Kai-ma.

Topographically, it is the land of *Mittelgebirge*, diversely crossed by ridges (Fig. 5), averaging less than 300 meters, excepting in the eastern and north-eastern portions from which the waters flow down to Korea Bay, through the channels of the Tai-dong Gang<sup>1)</sup> and the Chhyöng-chhyön Gang.<sup>2)</sup> As may be seen from their crooked courses, the rivers make their way through nearly reticulated ridges in diagonal directions. Especially the Tai-dong Gang serves for the

1) 大同江, a great-same-stream, or phai-syu (溟水).

2) 清川江

passage of waters from a great number of tributary rivers on the higher eastern level to the western lowland of Ph'yŏng-yang, which is at the same time the largest inland basin of Korea. The name Tai-dong Gang itself signifies a great confluent stream.



Scale 1:750,000. Vertical  $\times 2$ .

Fig 5.—Profile from the free port of Gen-san (Wŏn-san) to that of Chin nam pho in the Yellow Sea through the old capital Ph'yŏng-yang and the high pass of Ma-sing-nyŏng (1020 m.). This cross-section shows clearly the *Mittelgebirge* character of the *Paleo-Chyo-syŏn* land, rising higher as we go eastwards towards the Sea of Japan. The profile goes through the narrowest part of the peninsula; and we have to cross the lengthwise ridges during a traverse from the shore of the Yellow Sea to that of the Green Sea. They are the ridges of the Yuk-chyang near Kang-dong, the Mal-mŏri, the Chin-kokai, the A-ho-bi-nyŏng and the Ma-sing-nyŏng.

A mythic personage, Tan-gun,<sup>1)</sup> the father of the Korean kings, came down to the top of Myo-hyang-san, already mentioned, and at first chose Ph'yŏng-yang<sup>2)</sup> for the capital of the Tan-gun Chyo-syŏn<sup>3)</sup> dynasty. This was followed by the Keni-si Chyo-syŏn<sup>4)</sup> and Ui-si Chyo-syŏn<sup>5)</sup> dynasties. Their domains embraced the Intersertal and a part of South Manchuria. As the Koreans now call these old dynasties (B.C. 2317–209) collectively *Ko-chyo-syŏn*,<sup>6)</sup> I will hereafter speak of the realms of these old kingdoms *the land of Paleo-Chyo-syŏn*.

The region is mainly built up of granitic rock and grey thinly-tabular limestone, which complex is, geologically speaking, *shattered* into diverse blocks. The downthrows are of nearly the same magnitude, and during my flying visit it was extremely difficult to decide which had the priority and which the supremacy over the other. The results of the shattering are, of course, detached blocks,

1) 檀君.

2) 平壤.

3) 檀君朝鮮.

4) 箕氏朝鮮.

5) 衛氏朝鮮.

6) 古朝鮮. Under the Chinese rule, the region was called *Nang-mang* (樂浪).

but many of these often have slowly undulating *folds*. Perhaps it will be convenient for descriptive purposes to group the fault-ridges into two series—the *lengthwise* and *crosswise* ridges. In the following I shall select and characterize a few of the principal ones.

There are about seven *lengthwise* ridges and an equal number of *crosswise* ones. Counting from the south we have in the *south group of the latter series* the following :—

a) CROSSWISE SERIES.

*South Group.*

i. *The Syu-yang-san Ridge.*—In the southern Hoang-hăi Do we meet with this ridge with the scarp on the south, which starts from Syu-yang-san<sup>1)</sup> near Hăi-jyu<sup>2)</sup> and reaches Chhi-ak-san<sup>3)</sup> of Păik-chhyôn.<sup>4)</sup> The ridge of gneiss-granite is clearly seen from the south coast, and passes through Syong-ak-san<sup>5)</sup> of Syong-do.<sup>6)</sup> I have crossed it near Sang-nyöng<sup>7)</sup> at the Im-jiu Gang.<sup>8)</sup>

ii. *The Myör-ak-san Ridge.*—This ridge forms the axis of Hoang-hăi Do with the scarp in the contrary direction, *i.e.* toward the north. Probably coming from Shan-tung, it enters the peninsula at Chyang-san-kot and is prolonged to Myör-ak-san<sup>9)</sup> in Syö-heung,<sup>10)</sup> terminating at the brink of the trench of Chyuk-ka-ryöng at Ko-am-san,<sup>11)</sup> west of Phyöng-gang.<sup>12)</sup> An easy road leads from the latter to Phyöng-san<sup>13)</sup> on the south side of the ridge.

iii. *The Chyo-il-lyöng Ridge.*—This ridge begins from a slate elevation between Hoang-jyu<sup>14)</sup> and Chyung-hoa,<sup>15)</sup> and passes with a

- 1) 首陽山
- 4) 白川
- 7) 朔寧
- 10) 瑞興
- 13) 平山

- 2) 海州
- 5) 松岳山
- 8) 臨津江
- 11) 古庵山
- 14) 黃州

- 3) 雄岳山
- 6) 松都
- 9) 滅惡山(綿岳山)
- 12) 平康
- 15) 中和

south scarp through the mica-schist pass of Chyo-il-lyöng<sup>1)</sup> (450 meters), on the north of Syu-an,<sup>2)</sup> ending at the boundary of the province on the top of Păik-nyön-dök.<sup>3)</sup>

The above *three ridges of the south group* all lie in Hoang-hăi Do, and trend from W.S.W. to E.N.E., corresponding to the axis of the *Shan-tung Peninsula*. The *north group* of this series, however, runs from W.N.W. to E.S.E., conforming itself to the coast-line between An-jyu and Wi-jyu.

#### *North Group.*

iv. *The Hoang-nyong Ridge.*—On the highway northward from Phyöng-yang, at the place called Am-chyöng-năi-uön,<sup>4)</sup> a low elevation of granite-gneiss stretches southeastwards to Ku-Syang-uön<sup>5)</sup> on the way to the British mines of Ap-Eun-san. We meet with its south scarp at Hoang-nyong-san<sup>6)</sup> at the back of Kang-dong<sup>7)</sup> on the way to the east coast. I have crossed it at Mun-hön-kokăi,<sup>8)</sup> but could not trace its eastern course.

v. *The Mal-mok Ridge.*—Beginning again on the highway of Phyöng-yang on the north of Suk-chhyön,<sup>9)</sup> we have to ascend the two low kokăi or passes of Sai-nön<sup>10)</sup> and Păiam-kokăi.<sup>11)</sup> The ridge proceeds E.S.E., with a north scarp through Keum-san. At its northern foot is located the Gwendoline<sup>12)</sup> Mine of the British Mining Concession. I have crossed it on its easterly course at Mal-mok-kokăi,<sup>13)</sup> north of Syöng-chhyön,<sup>14)</sup> and followed its north foot to Yang-dök<sup>15)</sup> in my journey to the east coast.

vi. *The Thyön-syön-san Ridge.*—From An-jyu this ridge runs

1) 朝日嶺

4) 岩赤川院

7) 江東

10) 新院

12) The Koreans call the mine Yong-hoa-bang (龍化坊)

13) 馬項峴

2) 遂安

5) 舊祥厚

8) 文靈峴

11) 蛇峴 (暗雲峴)

14) 成川

3) 百年峯

6) 黃龍山

9) 肅川

15) 陽德

parallel to the preceding, but with a south scarp, through Syung-hoasan<sup>1)</sup> and Thyön-syön-san,<sup>2)</sup> the latter is clearly seen from the British mine. I have crossed it at Mi-reuk-kokäi<sup>3)</sup> (300 m.) on the way to Tök-chhyön.<sup>4)</sup> The ridge probably proceeds toward Wön-san and forms the boundary of Phyöng-an Do and Ham-gyöng Do. A low series of hills belonging to this line, is also observed along the coast, west of the Chhyöng-chhyön Gang which is greatly deflected in its upper course by this ridge.

vii. *The Tu-kai Ridge.*—This is the last and the northernmost of the series, presenting a somewhat anomalous situation in regard to its trend. It runs rather in the Liau-tung direction from Kai-chhyön<sup>5)</sup> eastwards, and I have crossed it at the ottrelite-schist pass of Tu-kai-kokäi<sup>6)</sup>, north of Tök-chhyön.

viii. *The Mäing-jyu Ridge.*—This short but remarkable ridge is met with at the east end of the preceding, stretching in the *Sinian* direction. It forms the boundary of Phyöng-an and Ham-gyöng, and also the water-parting between the Chhyöng-chhyön Gang and the east coast. The crushed-granite pass of the Mäing-jyu-nyöng<sup>7)</sup> lies on this mountain, and is one of the principal roads leading from Yöng-heung<sup>8)</sup> to Yöng-nön<sup>9)</sup>.

### β) LENGTHWISE SERIES.

Corresponding to the seven *crosswise* ridges just mentioned, we have an equal number of *lengthwise* ones which trend in the *Korean* direction, but they can not easily be brought into harmony with the *Thai-Pük-san Range*. They seem in a great measure to determine the coast line of the western shore of Korea. There are four principal and

1) 崇化山.

4) 德川.

7) 孟州嶺.

2) 天仙山.

5) 价川.

8) 永興.

3) 龜勒峴.

6) 斗介峴.

9) 寧遠.

three secondary *lengthwise ridges*, which, when counted from the west, are the following :—

i. *The Ku-uöl-san Ridge*.—From Kang-nyöng<sup>1)</sup> in Hoang-hăi Do, a ridge runs northwards through Mi-reuk-kokăi<sup>2)</sup> to Song-ku-san,<sup>3)</sup> the counterpart of Ku-uöl-san. It reappears in the celebrated gneiss-mountain of Ku-uöl-san<sup>4)</sup> which is tilted up on its east side with a gradual slant to the west. After a short course it disappears in Korea Bay, coming up again at Thyöl-san, whence it follows the east side of the Wi-jyu highway.

ii. *The Chă-mo Ridge*.—Starting from Yön-an<sup>5)</sup> at the mouth of the Han river, this ridge runs parallel to the preceding, and crosses the highway of Phyöng-yang at Kôm-syu-yök.<sup>6)</sup> It lowers at the east of Phyöng-yang, becoming again a little higher at Ko-bang-san, and proceeds to An-jyu past the Chă-mo Castle.<sup>7)</sup> In West Kai-ma it goes through the west of Un-san and Tong-chhang,<sup>8)</sup> probably crossing the Am-nok on the west of Pyök-dong.<sup>9)</sup>

iii. *The Yuk-chyang Ridge*.<sup>10)</sup>—Starting at the mouth of the Yöi-syöng Gang,<sup>11)</sup> this ridge likewise goes northwards, crossing the highway at Chhya-yu-ryöng<sup>12)</sup> and stretching to Yuk-Chyang-kokăi at the boundary of Phyöng-an and Hoang-hăi Do. Its northern prolongation may be traced through Kang-dong, Eun-san, and Kai-chhyön.<sup>13)</sup> The northern arm of the Tai-dong Gang flows southward between this and the Chă-mo ridge. In West Kai-ma it passes on the east of Yöng-byön and crosses the Am-nok between Pyök-dong and A-i-jin.<sup>14)</sup>

iv. *The Mal-möri Ridge*.—This is the most important ridge in the Paleo-Chyo-syön Land. Beginning at Syong-ak and Tai-heung-san<sup>15)</sup>

1) 康翎.

4) 九月山.

7) 慈母山城.

10) 六將峴.

13) 价川.

2) 彌勒峴.

5) 延安.

8) 東倉.

11) 禮成江.

14) 阿耳鎮.

3) 透九山.

6) 劍水驛.

9) 碧潼.

12) 車踰嶺.

15) 大興山城.

near Syong-do, and proceeding northwards, it forms the water-divide between the Im-jin Gang and the Yöi-syöng Gang. It crosses the Phyöngan-Wönsan road at the east of Ka-chhang where it culminates at Mal-möri<sup>1)</sup> and A-mi-san<sup>2)</sup> with a sharp fault scarp on its east side. I did not lose sight of the ridge till I had reached Tök-chhyön in the upper Tai-dong Gang. The upper Chhyöng-chhyön Gang cuts across the ridge at the curve of Syöi-göri,<sup>3)</sup> east of Heui-chhyön, and the ridge attains its greatest altitude in the majestic forest-covered Mur-i-san<sup>4)</sup> (1600m.). This granitic ridge is both the highest mountain in West Kai-ma and also an important watershed in the meridional direction.

v.—vii. The *remaining three ridges* are all parallel to one another and are rather insignificant as compared with the preceding four lines. We traverse them on the highway between Phyöng-an and Wön-san. They are the *Chün-kokäi* (500 m.), the *A-ho-bi-nyöng* (760 m.), and the *Ma-sing-nyöng* (1020 m.), the last is in reality a double-ridge, and is easily seen from Wön-san. (See Fig. 5, p. 45.)

1) 馬項

2) 峨眉山.

3) 細街.

4) 勿移山.



## IV. CONCLUSION AND SUMMARY.

In recapitulating what has been stated in the foregoing pages, I must first of all say that the geological-structural lines upon which the present paper has been woven, may not be entirely intelligible to the reader without some prefatory geological description accompanied by a geologic map. Some may even cast doubt upon my statements which, of course, must await verification by future observers. In regard to the geology of Korea, I hope I shall be able within a few months to give general outlines with an account of the geological history of the peninsula.

Korea is, as I have said, the Italy of Eastern Asia jutting out southward from the main body of Manchuria, just as Italy does from the other end of Eurasia. It is limited on the north by the equatorial chain of Chyang-päik-san which is looked upon by the Koreans as an offshoot of the great Kuen-lun, after being interrupted in its eastward course by the depression of Lian-tung at I-wu-li-shan. On the southern foot of the Chyang-päik-san range lies the basin of the Am-nok and Tu-man Gang which are separated from each other at Hyöi-sannyöng (700 m.) by a lava-flow from Päik-tu-san, the highest point (8,900 feet)<sup>1)</sup> of the Chyang-päik and the cradle<sup>2)</sup> of the Korean nation. The Alps and the plain of the river Po are the counterparts of these in the Italian peninsula. They lie nearly in the same latitude, enjoy a

1) 8,025 ft. in James' *The Long White Mountains*, p. 262.

2) "The sacred importance of the White Mountains has been recognized in the Far East for ages. They are first heard of under the name of *Bu-khian-san* (不咸山) [see ante 6]; a name not of Chinese origin, but reminding one of the Mongol Burkhan, as the Gentehi Mountains in Mongolia (according to some, Khan-ohi at Urga) were called in ancient times." "... in the *Chan-hai-king* (山海經), or book treating of seas and mountains, it is called *Pan-hien-chan*." [This seems to be misspelled. B. K.] As to the Chinese mythological history of the White Mountains, I refer the reader to the paper by the Archimandrite Palladius (*Expedition through Mongolia*), translated by Delmar Morgan. *Proceedings R. G. S.*, 1872.

favourable climate, and are inhabited by peoples of very ancient culture.

The peninsula is divisible on good grounds into two sections—North and South Korea—by a trench, in the geological sense, from the head of Gen-san harbour to Kang-hoa Bay, at one corner of which is located Che-mul-pho, the emporium and entrance to the capital, Seoul. This trench or rift-valley is lava-drowned (Pl. I, Fig. 3) and is the only extensive volcanic field in South Korea, except the large basaltic island of Chyöi-jyu (Quelpart) off the southern coast of Chyöl-la Do. This rift-valley or *Graben* of Chyuk-ka-ryöng (510 m.) affords the easiest passage obliquely across the peninsula from the Sea of Japan to the Yellow Sea, and marks the boundary of various geographic elements:

a) Historically, North Korea is the land of *Old Chyo-syön*. The dynasties founded by Tan-gun, Keui-chă, and Ui-man under the name of Chyo-syön, and Ko-ku-ryö or Ku-ryö founded by Chyu-möng, all had their domains mainly in this portion of the peninsula. At a somewhat later time in South Korea sprung up the First Three Hans—Ma-han, Sin-han and Pyön-han, followed by the Second Three Hans of which Sil-la and Päik-chyöi occupied the south, and Ku-ryö only North Korea. From the historical point of view, South Korea is the land of the Hans.

b) Climatically, the North is cold while the South is mild; the latter produces the rice, which is the main staple of the country.

c) Topographically, the *Han-land* (South Korea) is hilly, though lofty mountains crown the high coast along the Sea of Japan, slanting gradually westward and disappearing under the shallow, turbid waters of the Yellow Sea. In *North Korea* we have the two topographic types of the Kai-ma plateau in the north (Figs. 3 and 4.) and the Paleo-Chyo-syön on the south (Fig. 5.), the latter being hilly land of

the type of South Korea though on the average considerably lower. Consequently, the land gradually rises towards the east and most of the large rivers, such as the Am-nok, Chhyöng-chhyön, Tai-dong, Yöi-syöng, Im-jin, Han-gang, Keum-gang and Yöng-san-gang empty into the Yellow Sea<sup>1)</sup>.

d) The physique and temper of the people in both halves differ in no small measures.

---

The peninsula of Korea presents most interesting problems in the arrangement of its mountains and in its underground structure. Professors F. v. RICHTHOFEN<sup>2)</sup> and C. GOTTSCHÉ<sup>3)</sup> have made an attempt at their solution. On my return home from Korea this year, I had the great pleasure of reading SUSS' *Antlitz der Erde*<sup>4)</sup> which was soon followed by RICHTHOFEN'S *Geomorphologischen Studien aus Ostasien*, I, II, and III. The former author scarcely touches our peninsula, while the latter lets his *Tungusic curve* pass through the brinks of the East Kai-ma Land as far as to Ho-do (Hwa-do) near Ham-heung, and makes the *Korean curve* start anew from here and go

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1) See Figs. 1 and 2 in p. 22; Figs. 3 and 4 in p. 40, and Fig. 5 in p. 45.

2) *Vide ante* p. 4. Whenever I read his work on China, I am impressed with the great skill with which he treats the difficult names of that country. The method of correctly writing and transliterating in Roman letters geographic names outside of Europe and America is a matter always confronted with many difficulties. F. v. Richthofen's monumental work: *China*, is in this respect the first of the kind in all geographical literature. His painstaking study of the local idiosyncrasy, combined with Sir Wade's system, eventually enabled him to give a true reproduction of the pronunciation of both the personal and geographic names of China. The nomenclature of that country, at least in the German-speaking circle, now seems to have been brought into uniformity by this great authority on the subject.

I experienced the same difficulty in Korea, that Richthofen had in China; for though the Koreans and the Chinese use the same ideographic symbols, yet they attach different sounds to them; just as in the case of one and the same character our own pronunciation differs from that of the Chinese. I was therefore obliged to compile with the help of Mr. Kanazawa, a list of about 3,000 Korean geographical names in the romanized form. This list, bearing the title: *A Catalogue of Geographical Names of Korea*, is now in press. A geographic map on the scale of 1 : 2,000,000 will come out within a few days bearing my system of transliteration.

3) *Loc. cit.* See page 4.

4) Band III, Part I.

around the outer side of South Korea as far as to the mouth of the Yang-tze-Kiang. The two curves are said to enclose the land that corresponds to the inner *Staffelland* of the Great Khingan (Hsin-gan) and Taipanshan in China. The peninsula seems to have interested our two masters almost as deeply as it has the political leaders of our times. Let me try to reiterate what has been said in the present paper in regard to the geomorphology of the peninsula.

i. Archaean formation composed, as elsewhere, of gneiss-granite, gneiss and mica-schists, is thrown into broad, undulating folds on the front side of the peninsula, in the western portion of the Han-land and Paleo-Chyo-syön, becoming steeper as we go south. The axis of folding stretches from S.S.W. to N.N.E., or S.W. to N.E. Two prominent crests of this type are the No-ryöng and Chhya-ryöng ranges which extend obliquely across Chyöl-la Do and Chhyung-chhyöng Do. Besides, many small swellings of the crust-surface can be seen in the Paleo-Chyo-syön Land, though deeply hidden under the mask of Paleozoic formation. Nearly half of the area of the peninsula is occupied by folds of this class. These specialized folds should be classed, according to my view, with the Sinian System of South China, as was originally intimated by PUMPELLE.<sup>1)</sup>

It is a well-known fact that F. v. RICHTHOFEN prolongs his ideal line of the Sinian System to the frame-work of South Japan, a view endorsed by Dr. E. NAUMANN,<sup>2)</sup> and the late HARADA.<sup>3)</sup> L. v. LÓCZY<sup>4)</sup> is, on the other hand, disposed to think that it is the Tching-ling-shan that is prolonged to South Japan through the Hwai Mountains and the mouth of the Yang-tze-Kiang where the Sinian System clings to

1) See *ante* p. 14.

2) *Ueber den Bau und die Entstehung der japanischen Inseln*, Berlin, 1885.

3) *Die japanischen Inseln*, S. 28.

4) *Die wissenschaftlichen Ergebnisse der Reise des Grafen Béla Széchenyi in Ostasien*, Bd. 1, 98.

it (*Anschmiegung*). But no one knows what became of them after they disappeared in the Tung-hai.

The broad belt of the Sinian System which obliquely crosses the Korean peninsula, if extended beyond the Tung-hai, will join with the mountains of South China, to which the name Sinian System was originally given by PUMPELY. Baron v. RICHTHOFEN's ideal line<sup>1)</sup> runs from South Japan to Fuchou and then goes along the coast of Fokien and Kwang-tung, as is well seen on H. FISCHER's map<sup>2)</sup> of East Asia. As may be seen on any tolerably good map of South China, a greater portion of the Sinian System, of which Ta-yü-ling<sup>3)</sup> forms the axis, enters the Tung-hai between Fuchou and Shang-hai, and its further prolongation will correspond well both in its direction and its breadth to those which I venture to call the Sinian folds of Korea.

It should be specially remarked that, if the Sinian System in Korea be prolonged to the north-east, a greater part of the folds will again unite directly with the tectonic lines of the Sikhota-alin, as they are given in Ivanow's work.<sup>4)</sup> (Pages 13-17.)

ii. The Sinian represents an old system of crustal folds in the peninsula; and contemporaneously with it or a little later, there was generated another system in the Liao-tung direction in the Kai-ma Land, which was posthumously faulted in serial order towards the south, producing the parallel ridges of Myo-hyang-san, Työk-yu-ryöng and Kal-eung-nyöng. These trend from W.S.W. to E.N.E. and form apparently the direct continuation of South Manchuria. The well-known Chyang-päik-san stretches, however, *east* and *west*, obliquely

1) *Die morphologische Stellung von Formosa und den Riukiu Inseln.* Sitzungsberichte der Kön. Preuss. Akad. d. Wissenschaften z. Berlin, 1902, S. 961.

2) E. Debes' *Neuer Handatlas.* No. 41.

3) 大庾嶺.

4) *La chaîne du Sikhota-Alin*, p. 112. Explorations géologiques et minières le long du Chemin de fer de Sibérie. Livraison XVI. St. Petersburg, 1898.

meeting the preceding in the basin of the Tu-man Gang. The upper Am-nok Gang drains the acute angled area between the two systems which are cut down crosswise by the Syo-Chyang-päik-san at the north-east coast of Ham-gyöng Do. (Page 34.)

iii. By the Korean System I mean that complex of uplifted edges and sometimes folds which run more or less in north-south direction along the long axis of the peninsula. It is so characteristic to the physiognomy of the land that even native geographers<sup>1)</sup> long before us recognized its great importance in the surface-features of the peninsula. It is also so peculiar to Korea that I know of no other mountains bearing the same trend as these in South-east Asia. I presume, however, that something like the *Korean direction* may perhaps be looked for beyond the Chyang-päik-san range in Kirin and also at the terminal portion of the long ridge of the Great Khingan. Also a part of Kyu-shu (Japan) may be within its reach.

Within the complex of the Korean System, there seem to exist *two natural subgroups* which are named respectively the Thai-Päik-san and the Syo-Päik-san.

a. The first constitutes the backbone of the peninsula extending from the south-east of Kyöng-syang Do toward the N.N.W., along the coast through Thai-Päik-san, O-däi-san and Keum-gang-san. After a short interruption it seems to stretch to Nang-nim in the Kai-ma Land which is separated by it into east and west halves, while at the same time it forms the boundary of Phyöng-an and Ham-gyöng. A sudden turn of the upper Am-nok,—the Angle of Mao-êrh-shan,—is probably due to its prolongation, while the axial trend of Kö-chyöi Island indicates how the mountains curve a little to S.W. on entering the South Korean Archipelago.

Five components of the Thai-Päik-san are the cliffs of tilted

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1) See *ante* p. 6.

blocks sweeping along the coast of the Sea of Japan, from which the right wing was successively thrown down to the sea-bottom, as if it originated in disjunctive faults as an after-effect of the piling and pressing up of Hondo (Japan) toward the Pacific Ocean. (Pages 17-22.)

b. The second or Syo-Päik-san subgroup is also composed of fault-scarps which trend south of south-west. This sub-group builds the water-parting and boundary-wall between Kyöng-syang on the one side and Chyöl-la and Chhyung-chhyöng on the other. Instead of maintaining the nearly parallel course of the members of the Thai-Päik-san, the four component-ridges of the Syo-Päik-san diverge from near the pass of Chhyu-phung-nyöng in feather form in South Chyöl-la Do. In its north-eastern course the Syo-Päik-san is cut off by the Thai-Päik-san, exactly as the fold-crest of No-ryöng, already described, which, however, differs slightly in direction and greatly in its structure from the Syo-Päik-san members. (Pages 22-26.)

iv. No less remarkable than the preceding is the direction of the *Han-san Range* which chiefly confines itself to the southern border of South Korea. It trends from W.S.W. to E.N.E.; and corresponds well with the north side of South Japan, but as regards its western prolongation it is no easy matter to conjecture what will be its probable continuation. I simply suggest the idea that we might look for its linear extension in the basin-ranges that govern the course of the Lower Yang-tze Kiang. These low ranges seem to belong neither to the Kuen-lun, nor to the Sinian. (Page 31.)

The Han-san Range resulted from a later geologic event than that which produced the Korean System. The former is composed of a number of tilted edges of faults which threw down block after block to the Southern Sea. The sea-coast is dotted with an innumerable number of islets and rocks, and describes complicated in-and-out

curves. These peculiar features which characterize the coast, are nothing more than the outcome of the joint-work of the orogenic movements that gave form to the Korean and Han-san ranges. The inlets are the remains of tectonic valleys, while the headlands represent the ridges. Especially remarkable is the narrow canal of the free port, Ma-san-pho which presents the outline of a compound cross with a single axis, due to the Korean and Han-san ridges which intersect each other on both sides of the entrance. (Pages 26-31.)

This is a special form (Pl. III, Fig. 2) which truly deserves an independent position in the list of many coast-types. I name this the *Nam-hǎi* type, as this special kind of coast-line is seen all along the shores of the *Nam-hǎi* or South Sea of South Korea.

v. A great number of small ridges or fault-scarps traverse like a gridiron the whole of Paleo-Chyo-syön. The region is somewhat similar in its geological structure to the western half of Shan-tung. Well-established rules can be scarcely discovered in the arrangement of ridges. The whole tract is broken up into a number of long orographic blocks, each being of old sedimentaries, mainly of grey tabular limestone. Each block is tilted along the long side with steep walls, while it slants gradually towards the opposite direction. Some of the *equatorial* ridges may be brought into connection with the tectonic line of Shan-tung, *e.g.*, Myör-ak-san of Hoang-hǎi Do, while others of the same group are difficult to correlate with any known system. *Meridional* ridges, though coinciding in direction with some of the Korean System, do not harmonize with each other in position, nor in magnitude of disturbance; the general plan of the west coast, however, seems to have been greatly influenced by them. (Pages 46-50.)

In short, the intercrossing fault-scarps of Paleo-Chyo-syön inserted between the Sinian and Liao-tung systems seem to be the



result of a passive movement and after-effect of the still greater tectonic disturbances which gave to the crust-block of the Korean peninsula its present form.

*December, 1902.*

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PLATE I.





FIG. 1.—THE CANYON IN THE DIAMOND MOUNTAINS.

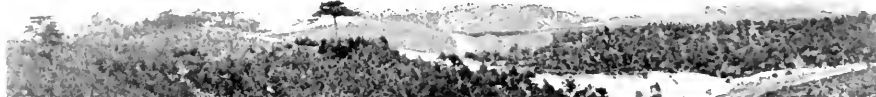


FIG. 2.—THE TAI-KOAL-LYÔNG RIDGE, RUNNING NORTH-SOUTH SEEN FROM THE EASTERN COAST.



FIG. 3.—BASALT PLAIN OF THIVÖL-UÖN, SEEN FROM THE NORTH, LOOKING DOWN THE MUSA.





PLATE II.





FIG. 1.—SURFACE-FEATURE OF THE BASALT PLATEAU, 1,700M. HIGH, EAST KALMA, SEEN FROM THE WESTERN MARGIN.



FIG. 2.—CANYON-LIKE VALLEYS IN THE SAME.



FIG. 3.—THE SMALL CHYANG-PAIK-SAN RANGE, ON AVERAGE 1,300M. HIGH, RUNNING NORTH-SOUTH, SEEN FROM SYU-SYŒNG, NORTH OF KYŒNG-SYŒNG.



PLATE III.





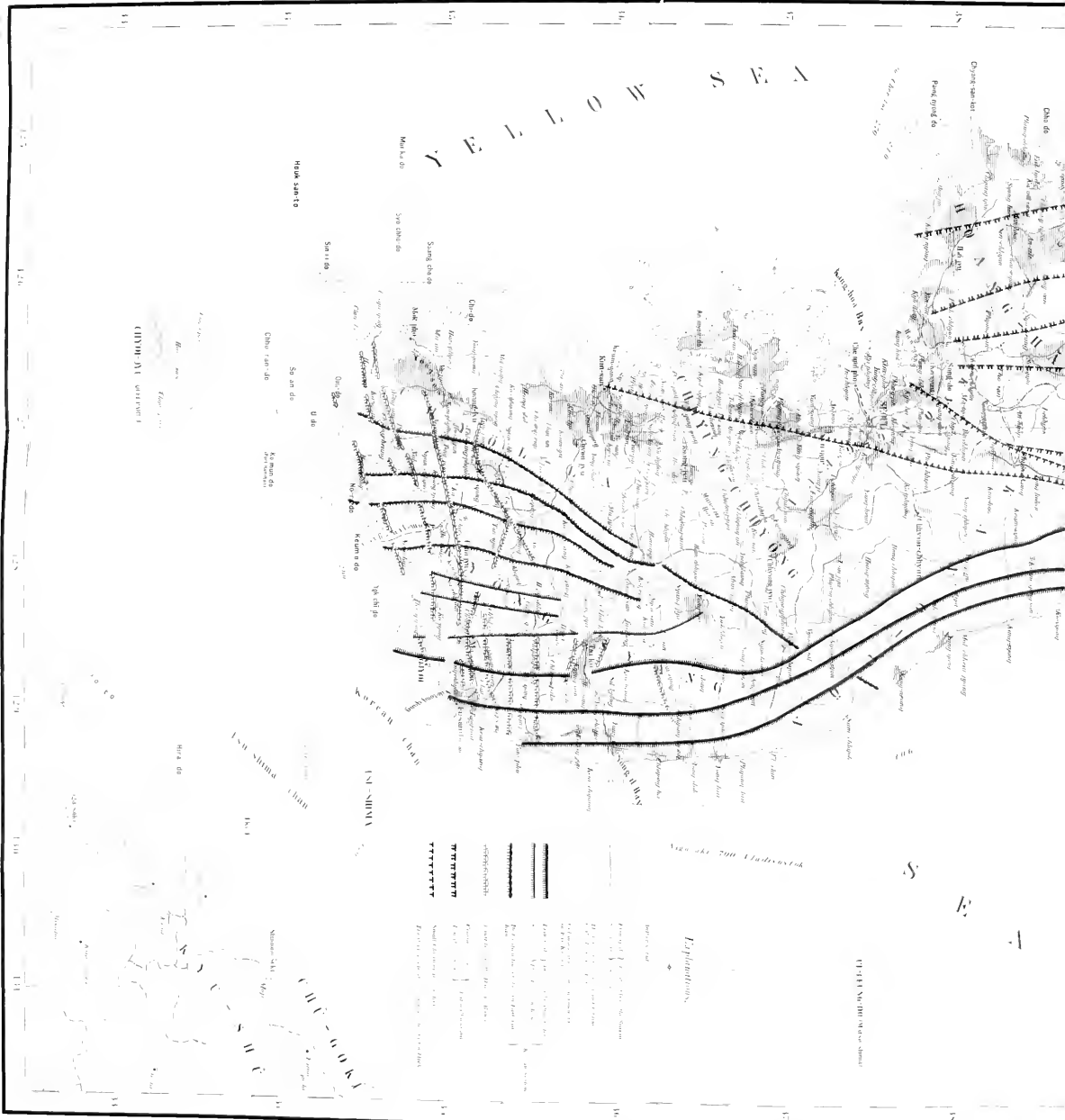
FIG. 1.—WESTERN VIEW OF THE NORTH END OF CHIRI-SAN, SEEN FROM THE HIGH FLAT OF UN-BONG.



FIG. 2.—THE DEEP INLET OF MA-SAN-PHO, LOOKING SOUTHWARD, SHOWING SMALL HEADLANDS JUTTING OUT FROM BOTH SIDES.



FIG. 3.—EXTENSIVE MUD FLAT EXPOSED DURING LOW TIDE, AT THE FREE PORT OF CHE-MUL-PHO.

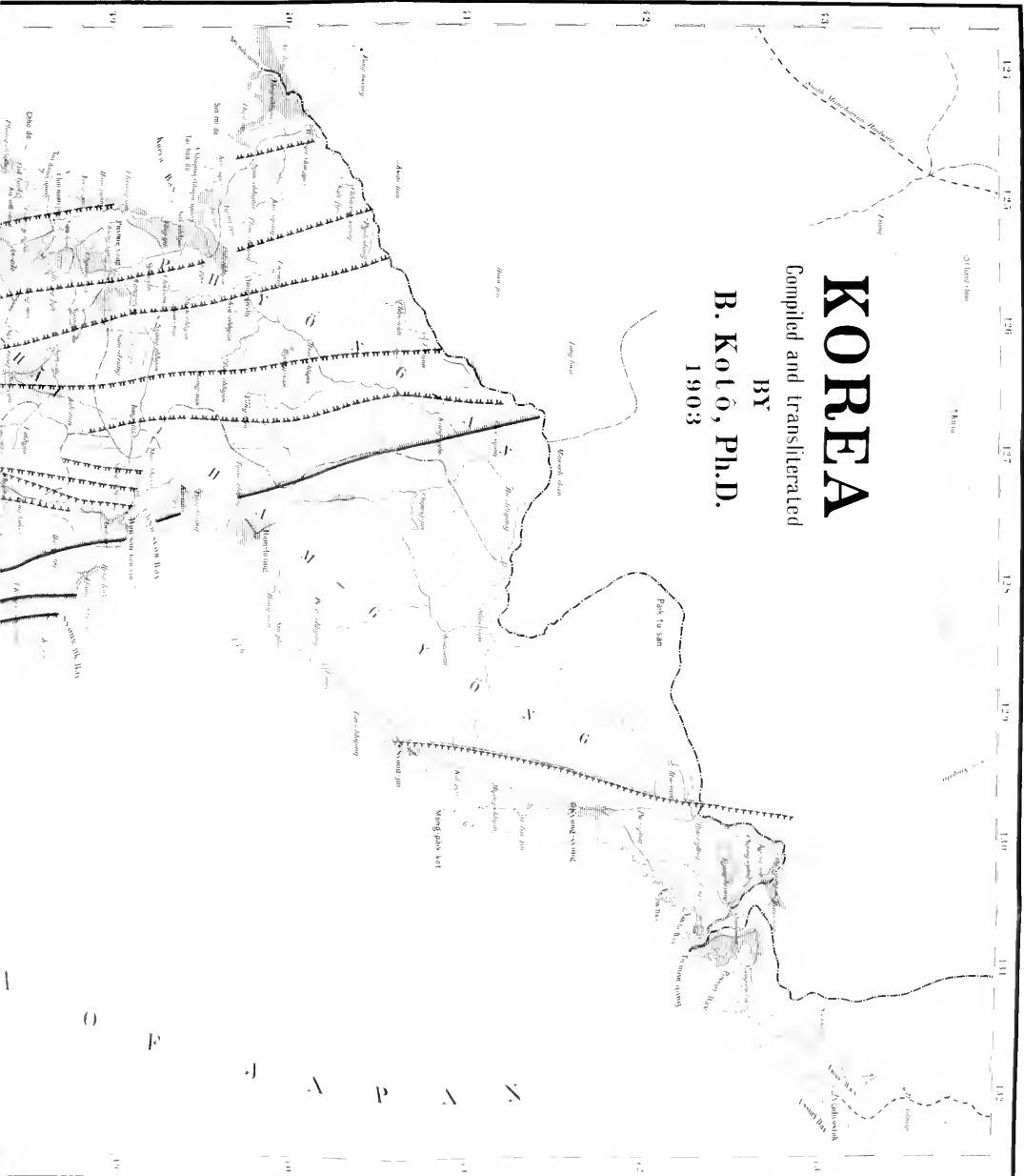




# KOREA

## BY

**B. Kolô, Ph.D.**  
1903





## Notes on Japanese Myxinoids.

A NEW GENUS *PARAMYXINE*, AND A NEW SPECIES *HOMEA*\*  
*OKINOSEANA*. REFERENCE ALSO TO THEIR EGGS.

By

BASHFORD DEAN.

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*With 1 Plate.*

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In the recent preliminary check list of the fishes of Japan by Jordan and Snyder, (1901, Tokyo, *Annotationes Zoologicae Japonensis*, Vol. III, Parts II-III, p. 126) two myxinoids are mentioned, *Homea burgeri* Girard, and *Myxine australis* Jenyns. The first represents the form described as *Heptatrema cirrhatum* by Temminck and Schlegel (1847, *Fauna Japonica: Poissons*): the second was identified, *vide* Dr. Günther, on the evidence of specimens taken by the Challenger on the "Hyalonema ground" off Misaki. In a subsequent paper Jordan and Snyder ("A Review of the Lancelets, Hag-fishes and Lampreys of Japan with a Description of Two New Species." *Pro. U. S. Nat. Mus.* Vol. XXIII, pp. 725-734, 1901.) describe the Japanese Myxine as a new species, *M. garmani*.

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\* Realizing that the time-honored name, *Idellostoma*, for this genus must be superseded I conclude with Mr. Garman that *Homea* (1822, Fleming) should be selected instead of a name prior by several years (1819, Duméril, *vide* Cloquet, *Dict. Sci. Nat.* XV, p. 134). To one who is not an out-and-out purist the earlier name "*Eptatretus*" to say nothing of its unaspirated condition.....is clearly a misnomer for forms which usually have not seven gill openings.

In addition to the myxinoids above referred to, the present writer during a stay at Misaki, as a guest of the Marine Laboratory of the Imperial University of Tokyo, was able to secure two undescribed species, one of which is remarkable for its large size, and in the possession of eight gill openings, the only myxinoid, indeed, in which this number is known normally to occur. The second presents characters closely transitional from *Homea* to *Myxine* and is regarded as representing a new genus. These forms are described on the following pages and reference is made to the eggs of three myxinoids and to the breeding characters of the common *Homea burgeri*.

The present studies were carried on largely at the marine station at Misaki, and partly at the Zoological Institute of the Imperial University of Tokyo. In both of these laboratories every facility was generously granted me, and I wish to acknowledge with especial gratitude the many courtesies of their director, Professor Kakichi Mitsukuri. My thanks are also due to Professor S. Watasé of the Imperial University, for his kindness in editing and publishing the present paper, favors which I especially appreciated in view of the difficulties attending proof-correction when an author is distant half way around the world.

### HOMEA BURGERI.

This species is taken in large numbers in shallow water in the small bays in the neighbourhood of the marine station at Misaki. Most of the specimens I examined were taken in water of three or four fathoms, and they occur in even shallower, for I have seen them near the stone steps of the laboratory. In this region specimens were obtained throughout the year, save during an interval of several weeks (September and October), when the fish were found to be

spawning. From my notes I give the following abstract relating to their life habits.

In the matter of feeding: They are not exclusively bottom feeders, for they found their way into a fish float which was anchored near the shore in a couple of fathoms water. And they here showed their predatory habits in a way which upon several occasions I would gladly have dispensed with. They would find their way into the float through crevices which seemed too narrow for their entrance, and they would attack and kill living fishes. I found that even electric rays, *Astrape dipterygia*, were not immune, for in several instances I detected hag-fish in the fish float side by side with these rays and noticed that the fin margins of the latter showed the rasped sores which are typical of the injuries caused by hag fishes. This is still another instance that even elasmobranchs are subject to their attack.\* The rays, it may be noted, were active, having been freshly caught, and were, one might reasonably conclude, well protected by powerful electric organs: to be sure, they were confined in a float, but it was of such a size as to give them plenty of room in which to move about: their only disadvantage was that they were unable to escape the continued pursuit of their enemies. That the hag-fish, moreover, exhibits to a greater degree than hitherto recorded, activity and persistence in pursuit of free swimming prey is more than probable from the following incident. According to Mr. Tsuchida, an assistant at the Misaki Laboratory, squid had often been successfully kept alive in a neighboring fish float: one night, however, living squid were confined in the float, but by some accident the lid was not

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\* This is mentioned, since it has been stated (Ayers, H., *Wood Hole Biol. Lectures*, 1894, p. 133) that these fishes are not subject to their attacks. I have already (*Kupffer Festschrift*, 1899, p. 224) noted the example cited by Johannes Müller. Dofflein has observed recently that a hag-fish entered the visceral cavity of a ray which was confined in the same pail.

tightly closed, and in the morning the float was found to contain several hag-fishes and the debris of squid. The conclusion is, therefore, that the squid had been caught while yet alive, in spite of their activity and keen nocturnal vision.

With a view of determining with some accuracy the sex characters

### Homea Burgeri: Table

Date.	Number examined	Percentages*			Size				Percentage having eggs of approx. uniform size.
		♂	♀	juv.	♂ max.	& min.	♀ max.	& min.	
1900.									
July 18.	37	63%	32%	5%	45-	30 cm.	45-	30 cm.	50%
Aug. 29.	41	83	14	3	54.5	29	45-	33	60
Sept.									
Oct. 28.	16	13	87	—	41.5	32	46-	32	63
30.	29	24	76	—	45-	29	46.5-	30.5	90
Nov. 25.	96	37	63	—	50-	28	60-	24	98
Dec. 15.	40	45	55	—	47-	29	47.5-	32	85
1901.									
Jan. 15.	33	45	55	—	48-	28	46-	30	95
Mar. 30.	96	31	65	4	47-	30	48-	32	81
June 5.	60	42	58	—	45-	31	45-	29	63
June 18.	14	60	40	—	49-	35	40-	37	83
June 30.	59	50	46	4	52-	30	50-	35	87
July 25.	91	78	22	3	54-	30	52-	27	80

\* Percentages are approximate. "Immature" specimens are

in this myxinoid, I took the opportunity of collecting an abundant material at various intervals during a period of somewhat over a year. In this time upward of six hundred specimens were examined, and from the notes made upon them, the following table was prepared.

### of Sex Characters.

Number of eggs of foregoing.			Size of eggs (mm.) of foregoing.			Remarks.
max.	min.	average	max.	min.	ave.	
23-	13-	18	23	22	22.9	{ Females with eggs either nearly mat- ure, or very immature (3 mm. or less).
24-	5-	15	25	22	23	{ Many large males, average size about 43 cm.
						{ 4 collecting trips: failed to get specimens.
27-	17-	23	—	—	—	{ Follicular capsules empty, from 9-12 mm. long.
—	—	—	—	—	—	{ All mature males spent. Follicular capsules empty.
—	—	—	—	—	—	{ Exceptions: 1 female, in which eggs measured 11-14 mm.
—	—	—	8	3	4.4	{ Exceptions: 1 female, in which eggs measured 12 mm.
—	—	—	7.2-	2-	4.2-	{ 1 female: eggs 2 mm....2 females: eggs 5 mm. rest bet. 7-14 mm.
30-	2-	17	20-	5-	11.9	2 females: 5 and 4 mm.
24-	5-	17	22-	16-	18.9	1 female: small eggs.
18-	9-	14	23-	3-	20	6 females: small eggs.
27-	4-	17	23	-19-	20+	1 female: small eggs: 1 male ripe.
32-	10-	19	25	-3-	22	

those in which sex could not be distinguished macroscopically.

From the foregoing data, we can, I believe, conclude very definitely that in the case of one myxinoid at least, a definite period of spawning occurs.\* For it will be seen that a very large proportion of the full grown females taken during the year are with eggs of a uniform degree of development. Furthermore, during the late fall it is found that nearly every full-grown female taken presents empty follicular capsules. And finally there can be traced a regular growth in the size of the ovarian eggs from the winter months to the late summer. Exceptions to these rules undoubtedly occur, but they are, as the table shows, far from common. The rate of growth of the egg in length is estimated approximately at 3 mm. per month. It may be safely said that the ovarian eggs begin to differentiate distinctly during the month of January, and that their growth (in length) is completed by the middle of August. The spawning season appears to the last from about this time until the end of October. By the middle of the latter month, however, more than half of the females appear to have spawned. By the end of November the spawning season is probably finished. I have noticed also that the sexual development of the male corresponds in general with that of the female. All males taken at the end of October were completely spent. Those taken during July showed clearly late stages in spermatogenesis, and ripe specimens were not uncommon.

As in the case of the Californian myxinoid, *Hømea stouti*, there can be little question that in the Japanese species, too, hermaphroditism does not occur, to say nothing of its protandric form. At certain seasons of the year, however, males are uncommon, and in certain

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\* It is by no means impossible that a systematic examination of other myxinoids will yield a similar result, although it cannot be denied that some spawning may occur all the year around. In *H. stouti* there is also evidence that the greater number of females deposit their eggs at nearly the same time.



localities it is probable that female specimens may alone be taken. That this condition sometimes occurs I have the testimony of Dr. P. Schmidt of the Fishery Board of the Russian Government, who informs me that during his stay at Kagoshima, he had an excellent opportunity of examining this myxinoid and that among the many specimens taken he was unable to discover a single adult male. In further detail : The males are taken in greater and greater abundance from March until breeding time, when they are about three times as plentiful as females. In the fall, on the other hand, the relative abundance of the sexes is more than reversed, six times as many females having been taken toward the end of October. From this time onward, with the exception of an inconsiderable fluctuation during the spring, males increase and females decrease in number in the catches, until spawning time occurs again. The great catch of females during the period immediately after spawning attests either that these fish have not taken food for a long period, or that they then require an exceptional amount of food to condition them for the task of resorbing the empty ovarian capsules and of initiating the growth of the eggs of the new season, or, possibly indeed, both causes may have operated. In regard to the proportion of the sexes taken during July and August, I may note that I have found similar results on the Californian coast in the case of *H. stouti*, in a tabulation of three hundred and fifty odd dissections. It is noteworthy that small, sexually undifferentiated specimens were rarely taken at Misaki, scarcely two per cent. of all material examined. In regard to the size relations of the sexes, furthermore, the present observations are closely in keeping with those which the writer has made on the Californian species. The largest specimen recorded was a female measuring 60 cm. in length ; and the largest male measured 54.5 cm. On the other hand, the average size of one hundred males,

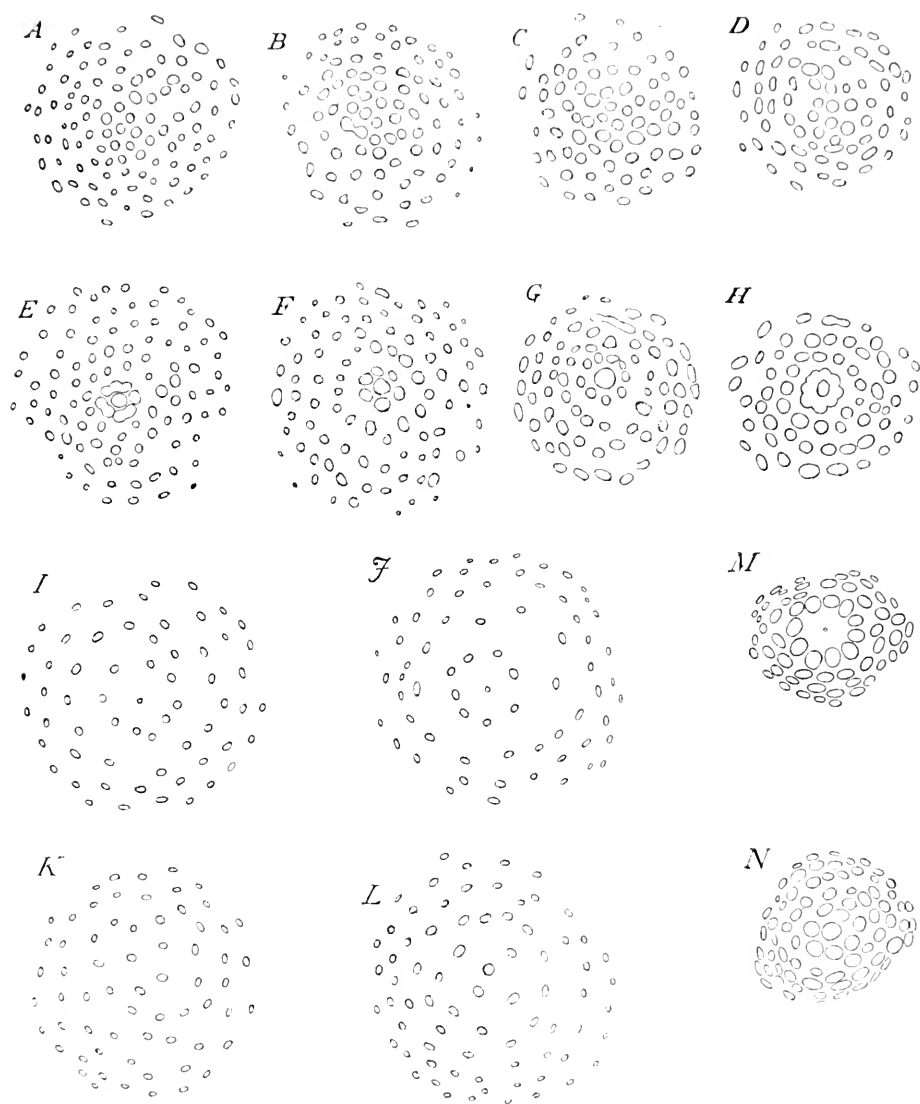
taken at random, was found to be 42 cm., and of one hundred females 41 cm. In general the largest males are more abundant than the largest females. The average number of eggs in the species is computed to be eighteen (in 400 individuals). The length of the egg at the time of spawning measures about 22 mm. not including the terminal filaments. An opercular ring is occasionally present at the vegetal pole. The anchor filaments are more numerous than in any known myxinoid, 100 or more being often present.

The egg of this species is shown in Pl. I. Fig. 7, and may be compared with those of other Japanese myxinoids figured in the same plate. In Text-figure 1 is shown the pattern formed by the bases of the anchor filaments in the case of four eggs selected at random: at the vegetal pole (*A, B, C, D*) the number of filaments varies between 91 and 72, at the animal pole (*E, F, G, H*) between 119 and 67. The average of ten specimens examined is 79 and 88 respectively. Surrounding the micropylar funnel the first ring of filaments is made up of eight (average) components and they are situated close to the micropyle.

As far as the chances of obtaining embryonic material is concerned, I have no doubt that a determined effort would procure eggs in the neighborhood of Misaki as readily as on the Californian coast. And I may add that while absent from Misaki during the late fall, specimens were secured for me which yielded eggs in the same manner as those obtained in California. On that occasion more than a score of eggs were taken from the slime enclosing a captured hag. It is probable that some of these eggs, if not the majority of them, had first been in the fishes' gut.

#### HOMEA OKINOSEANA, n. s.

Of this species I have examined three adult specimens, two



**Text Fig. 1.** A—H, Pattern formed by bases of anchor filaments of the eggs of *Homoea burgeri*.

A, B, C, D. At vegetal pole of egg.

E, F, G, H. At animal pole of egg.

I—N, Pattern formed by bases of anchor filaments of the eggs of *Homoea okinoseana* (I—L), and *Paramyzine atami* (M, N).

I, J. At animal pole.

K, L. At vegetal pole.

M. At animal pole.

N. At vegetal pole.

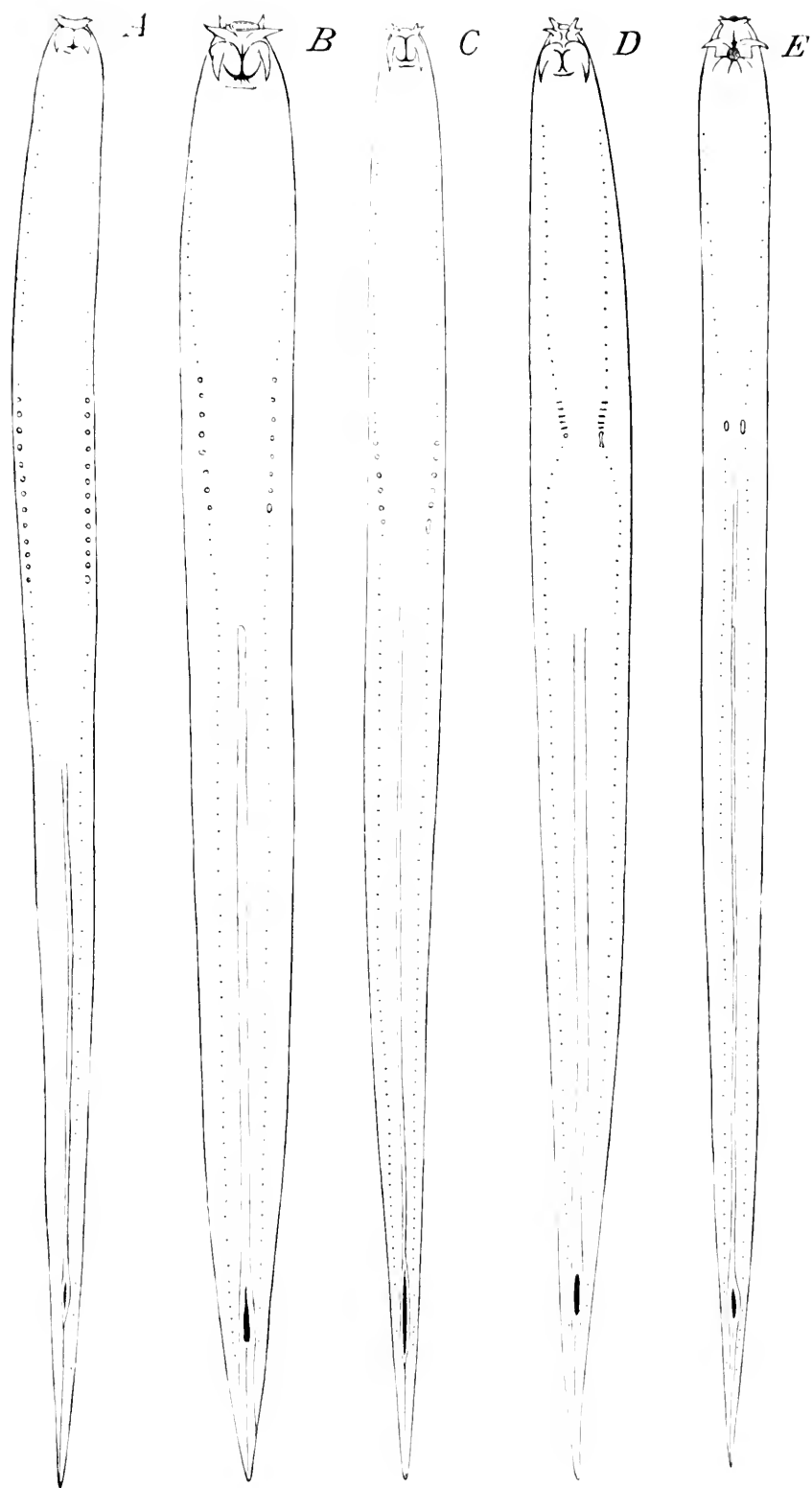
males and a female. The former measures 64 and 70 cm. the latter 80 cm. I learn, however, from Kuma Aoki, the skilful collector of the Misaki station, through whom I secured the specimens, that this species is not uncommon in the region "Outside Okinosé." Okinosé,\* it may be remarked, is one of the well-known fishing banks off the mouth of the bay of Tokyo, long famous as a collecting ground of glass sponges. The southern end of this bank deepens suddenly from forty to about three hundred fathoms, within a surface distance of about a kilometer. The present specimens were taken in water of four hundred fathoms in a tract well known to the fishermen by a name equivalent to "myxine ground." Kuma tells me, furthermore, that this particular species is in especial disfavour with the fishermen on account of the great amount of slime with which it befouls the trawl-lines. This can readily be believed, judging from the large size of the present specimens.

In point of size, if it is fair to conclude from but the three specimens examined, *H. okinoseana* is the largest myxinoid known. It is stout moreover in proportion to its length, as is shown in the accompanying figures (Text-figure 2, *A—E* p. 11),† of five species of myxinoids, which have been drawn in ventral aspect and reduced to a common scale. In each of the three specimens examined, eight branchial openings are present on either side. And in each case, as dissection shows, the eighth branchial sac is present on the left side, its outer duct merging into the ductus œsophagœus near its external

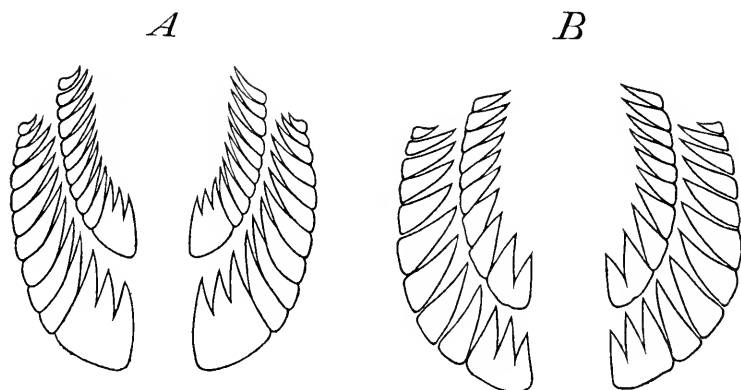
\* Cf. I. Ijima. Studies on the Hexactinellida. J. Sci. Coll. Tokyo. Vol. XV, 1901, p. 8.

† Text Figs. 2 Various myxinoids, ventral aspect, reduced to common length.

- A. *Homoea stouti* Lockington.
- B. „ *okinoseana* Dean.
- C. „ *burgeri* Girard.
- D. „ *Paramyxine atami* Dean.
- E. „ *Myxine garmani* Jordan and Synder.



opening. Accordingly in the numerical relations of the gills the present species fills up the gap which has existed between the bdellostomas with a small number of gills, *i.e.*, those of five and six (seven) gill-pairs, and those of many gills, from ten to fifteen. For in addition to the regular number of eight gills in the new species, we must include the ductus œsophagœus as representing on one side at least a ninth gill. Judging by the conditions in other hag-fish, moreover, I have no doubt that variations occur in the present species which would make the foregoing transition still more convincing. I



**Text Fig. 3.** Dental cusps of new Japanese myxinoids.

A. *Paramyxine atami*.

B. *Homœa okinoseana*.

note in this connection that a numerical variation occurs in the gills of *H. burgeri*. In as large a proportion as ten per cent. of the material examined, I find that the excurrent opening of the sixth left branchial sac opens to the surface in front of the ductus œsophagœus.

On Pl. I, Fig. 1 is shown the lateral view of this species. It has been drawn to scale so that the proportion of "head" and "trunk" can be estimated. By comparison of Text-fig. 2 *B* with Text-figs. 2 *A*, *C*, *D*, *E*, it will be seen that the outer gill openings

are situated somewhat further forward than in *H. burgeri*. I note that a well marked median ventral "fin" is present, and that the dorsal finfold is restricted to the region of the tail tip.\* The dental formula in two specimens was  $\frac{1}{1\frac{1}{2}} | \frac{1}{1\frac{1}{2}}$  of the third  $\frac{1}{1\frac{1}{2}} | \frac{1}{1\frac{1}{2}}$ . The more median teeth on either side are confluent at their bases, three of the outer and two of the inner rows. (Cf. Text-fig. 3 B). The base of the tongue extends backward between the second and third pairs of branchial sacs; the afferent artery, however, divides opposite the seventh pair. The lateral mucous pores are dark-colored and inconspicuous. The color of the present species is dark purplish brown.

In the female specimen above referred to the ovary contains 44 eggs. These are in a late stage of development and enable us to determine with reasonable accuracy the size of the egg at maturity together with the number of the anchor filaments. I find, accordingly, that the length of the egg averages 35  $\mu$ m., its diameter 12  $\mu$ m., its general shape and its actual length being indicated in Pl. I, Fig. 2. In two specimens examined by Mr. Naohidé Yatsu, who kindly prepared Text-Fig. 1, p. 9, the number of filaments at the animal pole were 62 and 63 and at the vegetal pole 64 and 74. (Text-fig. 1, I—L). It is possible, however, that the number of filaments in these eggs was not yet completed. The figures indicate that the central ring of filaments surrounding the micropylar funnel (I—J) is of greater diameter relatively than in other myxinoids described.

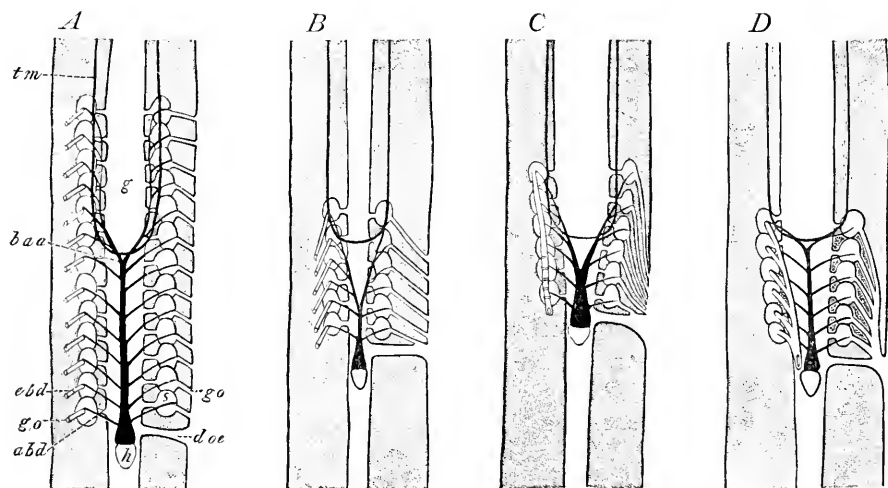
Two of the types are preserved in the Museum of the Science College of the Imperial University of Tokyo, the third in Columbia University, New York City.

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\* The anterior extension of these fins is somewhat variable, depending upon the amount of blood which their sinuses contain.

**PARAMYXINE ATAMI**, nov. gen., nov. sp.

The single specimen upon which the present description is based was obtained in water of 270 fathoms off Cape Manazuru, near the famous hot springs of Atami (Izu : Sagami Sea), a local name which may appropriately be used to distinguish the species. Kuma Aoki, by whom the specimen was collected, tells me that it is the first which he has seen during his many years fishing and collecting.



**Text Fig. 4.** Diagrams of brancial regions of various myxinoids. Ventral aspect. In each the branchial ducts appear at the left in their normal position, at the right schematized so as open directly lateral.

A. *Homea stouti* Lockington.

B. *Homea burgeri* Girard.

C. *Paramyxine atami* Dean.

a. b. d. afferent branchial duct.

b. a. a. bifurcation of afferent aorta.

d. oe. ductus oesophagus.

g. gut.

g. o. gill opening.

h. heart.

s. gill sac.

t. m. dark line showing position of tongue muscle.

The type, a female, measures 55 cm. in length. It is preserved in the Imperial University of Tokyo. On a following page (p. 22) are given the distinguishing characters of this genus and species. I note, however, that the figures drawn by Mr. Kuwabara,



given in Pl. I, Figs. 3 and 4, give a good idea of its external characters : also in Text-fig. 2 of its proportional measurements in terms of other species. Its "teeth" are shown in Text-fig. 3 *A*. And in Text-fig. 4 *C* a diagram indicates the relations of the branchial ducts and the afferent vessels. Its egg is figured in Pl. I, Fig. 5, and the arrangement of its anchor-filaments at either pole is shown in Text-fig. 1 *M*, *N*. In this myxinoid the pointed shape of the head and the close approximation of the external gill openings suggest closely *Myxine*.

#### MYXINE GARMANI, JORDAN AND SNYDER.

All specimens of this species recorded were taken in the neighborhood of the mouth of the bay of Tokyo. The most famous *Myxine* ground appears to be the one situated in Outside Okinosé. It is from this region, or near it, that the specimens of the *Challenger* were obtained. I have received five specimens from this region, of which three were immature, measuring about 35 cm. in length. The species is a large one, its adult averaging about 50 cm. Its color is dark indigo purple, somewhat bright in tone.

In distinguishing this species from *M. australis* Jenyns, to which Günther referred it, I add to the reasons adduced by Jordan and Snyder the following :—

It is a larger species, its dental cusps are more numerous and the base of the tongue muscles extends further tailward than the first pair of gills. The more median dental cusps fuse as in the southern Pacific species, but they are smaller than the more lateral ones. A more definite comparison of the normal of this species with the normal of the southern Pacific one, may render it advisable to regard the Japanese form as a variety of *M. australis*, but the differences as above pointed out, viewed in connection with the emphatic geographic-

al distinctness of the two forms, are at present I believe sufficiently striking to warrant the creation of a new species.

### GENERAL CONSIDERATIONS.

As far as our present knowledge goes, Japan is the most favorable region for the study of myxinoids. In no other known locality are four species, representing three genera of these important chor-dates, found living practically side by side,—for in the neighborhood of Misaki they occur within a distance of 30 kilometers. Here too, a form of myxinoid can be obtained in greater abundance than in any locality known to me, and there is also a promising field\* for collecting developmental stages. Hitherto the bay of Monterey has provided all myxinoid embryos recorded, but in the latter locality, one may add in parenthesis, the collection of hag-fish eggs has been due to the labors of practically a single fisherman, Ah Tack Lee, whose energetic help is thus almost a *sine qua non*.

It was especially interesting to me to ascertain that the relations of sex in *Hemica burgeri* were in every way similar to those of the Californian *H. stouti*, in spite of the fact that the former represents a a six and the latter a twelve-gilled form. Accordingly, realizing that the only conspicuous structural difference between *H. burgeri* and *Myxine* is in the matter of the position and confluence of the outer ends of the branchial ducts, the number of the gills being the same—there seems less ground than ever for attributing to *Myxine* protandric hermaphroditism. The authors who maintain this, Cunningham and Nausen, have to my mind been so unfortunate as to have collected their specimens in a locality where females alone were abundant

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\* I have since learned that Professor Hattai deserves the credit of being the first scientist to obtain embryos of a myxinoid. In the early nineties he was successful in obtaining eggs and embryos of *H. burgeri* in the Bay of Tokyo, not far from Omori.

among adult specimens. And in order to account for general absence of full-grown males, they have concluded that the females had in earlier condition been males. In support of this hypothesis they have found eggs in the anterior portion of the testis in certain of the immature males, a teratological condition which is now known to be not uncommon in other chordates. Perhaps in Japan an author might have fallen into a similar fallacy in examining *H. burgeri*, had his observations been carried on in the region of Kagoshima (Satsuma), according to Dr. Schmidt's observation already referred to. I confess, however, my suspicions that even in the localities in which Cunningham and Nansen collected, full grown males would be forthcoming in comparative abundance (both authors agreeing that full-grown males *do* occur occasionally), if a very large number of specimens are taken and at various seasons of the year. Neither author, by the way, as far as I am aware, has given any definite idea of the relative number and size of the specimens taken, or even of the total number upon which their generalization was based.

It is a significant fact that in practically the same locality there occur several forms of myxinoids. It affords, it seems to me, an additional support for the belief that the myxinoids are an ancient group, which has passed through a period of evolutionary prosperity, after the fashion of sharks, lung-fishes or ganoids, a belief which has already found favor by reason of their singularly wide geographical distribution. Garman, moreover, in his recent (1899) report on the fishes collected by the *Albatross*, has given important data which one interprets as bearing favorably upon this matter from the stand point of vertical distribution. And now in an especially conservative locality, as at Misaki, we can still catch a glimpse, so to speak, of the better days of the myxinoids, for here there are living side by side three distinct genera represented by at least four species.

The wide range in the variational characters in species of myxinoids has long been appreciated, in the matter, for example, of the number of gills and 'teeth' and in the proportions of body regions and fins. My own observations lead me to the belief that in the case of myxinoids it is peculiarly necessary to base specific determinations upon the average characters of as great a number of individuals as practicable. Unfortunately, but few specimens of the southern species have as yet been examined critically, and until the contrary is proven, we have, therefore, to accept their characters already described as representing the average for these species. As far as my own observations go, there is the greatest relative constancy in the position of the outer branchial openings, *i.e.*, in respect to their location dorsal or ventral, anteriorly and posteriorly, and as to the interspaces of the openings in each row. The relative length of the external portion of the branchial duct in the last as distinguished from the first gill pouches is also found to be notably constant. Dental characters present somewhat wide variations, although as far as numerical variations go, it is not difficult to obtain the normal for each species. In such a calculation the most troublesome question is to what degree immature 'teeth' should be counted:—or rather, the minimum size of those which must be taken into account. For one often finds at the posterior end of each row of 'teeth' several more or less minute cusps, which strictly speaking can be counted as 'teeth,' although not actually functional. And by reckoning or not reckoning these one would easily obtain the wide variations in a dental formula which Ayers, for example, has given for *H. stouti*. The fusion of the two or three cusps at the median end of each row of teeth appears to be moderately constant for the species. It certainly has no value, however, as a generic character, for we find that the same degree of

the fusion of these elements occurs in *H. burgeri* as in *Myxine*. As far as my observations go, furthermore, there is considerable constancy in the degree of bifurcation of the afferent aorta and in the degree to which the tongue muscle extends hindward, both characters measured with reference to the position of the branchial sacs. The number of the mucous pores, whether "pectoral" or "abdominal," on the other hand, appears to me of minor value: not only do they vary in number palpably, but the anteriormost as well as the posteriormost are very difficult to count, so that in a given specimen, one cannot I believe, conclude what the number is without allowing for a possible error of two or more on either side, a discrepancy which in many cases is sufficient to invalidate the usefulness of this specific test.

The character of the egg, on the other hand, is found of no little importance in determining species: for each species presents well marked differences in the number, size and shape of the eggs, and in the number and distribution of the anchor filaments at the poles.

The above considerations have, as far as possible, been taken into account in the case of two genera of Hyperotretes in the preparation of the following synopsis.

(Class) **MARSIPOBRANCHII.**

(Sub class) **HYPEROTRETA.**

(Order) **MYXINIA.**

(Family) **MYXINIDAE.**

(Genus I) **HOMEA** Fleming, 1822. *Phil. Zool.*, II, 374. (= *Bdelostoma*, Müller, 1834).

Hyperotretes with branchial apertures, six to fourteen in number, lateral of branchial sacs. Ectal efferent branchial ducts of approx-

imately equal length. Transverse muscles (branchial constrictors) situated along a considerable space ventrad of the gill sacs. Aperture of ductus œsophagæus somewhat larger than gill openings. (Cf. Text-fig. 4, *A*, *B*).

(Species I) **Stouti**. Lockington, 1878, *Am. Nat.*, p. 793.

Twelve gills (variations from 10 to 15). External branchial ducts short. Base of tongue muscles between fifth or six pair of gills. Dental formula  $\frac{10}{10} | \frac{10}{10}$  (variations from  $\frac{9}{9} | \frac{8}{9}$  to  $\frac{11}{11} | \frac{12}{11}$ ). Average size of adult (based upon 100 specimens) 42 cm. Brownish purple, with margins of branchial apertures and mucous pores white.

*Eggs* average 20 in number, each (all lengths here given not including filaments) about 23 mm. long by 8 mm. thick: anchor filaments average about 45 at animal pole, 35 at vegetal. Operculum almost invariably wanting near vegetal pole.

*Habitat*, Coast of California.

(2) **Polytrema**, Girard, 1854. *Pro. Acad. Nat. Sci. Phila.*, p. 199. (=Le Gastrobranche dombey (non-binomial), Lacepede, 1798. *Nat. Hist. Pois.* I, p. 531): (=bishoffi, Schneider.)

Ten gills (variation to 14). External branchial ducts short. Base of tongue muscles between seventh and eighth pair of gills (Putnam). Dental formula varies (Ayers) from  $\frac{11}{7} | \frac{11}{7}$  to  $\frac{13}{12} | \frac{13}{12}$ . Average size 45 cm.

*Eggs* in single instance—probably of *H. polytrema*—34 in number (Plate), measuring about 22.5 by 9.5 mm. Filaments at either pole about 80 and relatively long. Operculum common at vegetal pole.

*Habitat*, Coast of Chili.

(3) **Okinoseana**, *nov. sp.*

Eight gills. External branchial ducts short. Base of tongue between second or third pair of branchial sacs (afferent artery divides opposite seventh pair). Dental formula  $\frac{11}{12} | \frac{11}{12}$  ( $\frac{10}{12} | \frac{10}{12}$  in one speci-

men): three more median teeth of outer row, two of inner row confluent at bases: of these the median are the smaller elements. Average length of specimens (2 male, 1 female) 71 cm. Color dark purplish. Gill apertures and mucous pores obscure.

*Eggs* (in one specimen) 44 in number, averaging 35 mm. in length: about 12 mm. in thickness. Operculum at one pole only: filaments about 65 in number at animal, and 70 at vegetal pole. Innermost filamental at animal pole somewhat widely removed from the micropyle.

*Habitat*, Sagami Sea, Japan.

(4) **Cirrhata** Sch. 1801. (= *Heterotrema forsteri*).

Six (or seven) gills. External ducts slightly longer in anterior gills than in posterior. Base of tongue between first pair of gills. Dental formula  $\frac{10}{10} | \frac{10}{10}$  variation (Ayers)  $\frac{8}{7} | \frac{8}{7}$  to  $\frac{12}{11} | \frac{12}{12}$ . Average size about 48 cm. Coloration and *Eggs* undescribed.

*Habitat*, Coast of South Africa, and New Zealand.

(5) **Burgeri** Girard. 1854. *Pro. Acad. Nat. Sci. Phila.*, p. 199.

Six (variation seven) gills. External ducts somewhat longer in anterior gill than in posterior. Base of tongue between second (or first) pair of gills. Dental formula  $\frac{9}{9} | \frac{9}{9}$  variation  $\frac{8}{9} | \frac{9}{9}$  to  $\frac{9}{10} | \frac{9}{9}$ . Largest (median) three teeth of outer row confluent at bases, largest two teeth of inner row also. Average size 41.5 cm. Light brownish purple, unpigmented median dorsal band.

*Eggs* average 18 in number, each about  $22.4 \times 8.6$ , averaging 90 filaments at animal, 80 at vegetal pole. Operculum not uncommon at vegetal pole—in my material in 5 specimens out of 20: in none, however, is the opercular line sharply marked, altogether complete, or situated at any distance from the marginal filaments. Innermost filaments at animal pole located close to the micropyle.

*Habitat*, coast of Japan.

(Genus II) **PARAMYXINE**, *nov. gen.*

Hyperotretes with branchial apertures ventrad of sacs. Ectal branchial ducts of distinctly unequal length, the most anterior several times the length of the most posterior. The duct of the most anterior gill opening at the surface opposite the fourth (or fifth) gill sac. Openings of branchial ducts drawn close together and compressed transversely, that of the ductus œsophagœus, however, longitudinally, the latter aperture of large size, its length equalling that of the sum of the interspaces of several gills. Transverse constrictor muscles of the branchial region developed as a distinct element in the region of the hindmost branchial sacs. (Cf. Text-fig. 4, *C*).

(Species I) **Atami** *sp. nov.*

Six gills. Ectal duct of the most anterior gill three or more times the length of the most posterior. Base of tongue muscles between third pair of branchial sacs. Dental formula  $\frac{1\frac{3}{4}}{1\frac{2}{4}}$ . Three teeth, the most nearly median of each row, confluent at bases. Length about 55 cm. Dark purplish : gill apertures white : mucous pores conspicuous and dark colored.

*Eggs* in type specimen 25 in number, each about 30 mm. by 8 : narrow, therefore, and long : blunt ends. In two similar eggs taken separately on trawl line measurements are 30 by 7. No opercular ring at vegetal pole. Filaments about 75 in number at either pole, arising close together. The inner circle of filaments at animal pole separated somewhat widely from micropyle.

*Habitat*, Sea of Sagami, Japan.

(Genus III) **MYXINE** Linné. 1754. *Mus. Ad. Fridr.*, I, p. 91.

(Cf. esp. German, 1899, (Fishes collected by the *Albatross* pp. 342-350).

Hyperotretes with but a pair (variation one and one half pairs)



of external openings of the branchial sacs. The latter six in number, their outer ducts confluent. Distinct transverse muscles present, constricting branchial region. (Cf. Text-fig. 4, *D*).

(Species 1) **Australis** Jenyns, 1842. *V. of Beagle*. Fishes. p. 159.

(Variety 1) *tridentiger* Garman, 1899. (op. cit. as *species*).

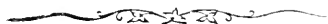
( „ 2) *acutifrons* „ „ ( „ „ „ „ ).

( „ 2) **Glutinosa** Linné, 1754. *Mus. Ad. Fridr.* 1, p. 91.

( „ 3) **Limosa** Girard, 1858. *Pr. Phila. Acad.* p. 223.

( „ 5) **Garmani** Jordan and Snyder, 1901. *Pro. U. S. Nat Mus.* p. 731.

( „ 6) **Circifrons** Garman, 1899. (op. cit.)





BASHFORD DEAN.

Notes on Japanese Myxinoids.

PLATE I.

## PLATE I.

- Fig. 1. *Homoea okinoseana*. ♂  $\times 2/3$ .  
2. *Homoea okinoseana*. Late ovarian egg;  $a$ , its actual length.  
3. *Paramyrine atami*. ♀  $\times 2/3$ .  
4. *Paramyrine atami*. Ventral view of head region.  
5. *Paramyrine atami*. Naturally deposited egg;  $a$ , its actual length.  
6. *Myrine garmani*. Late ovarian egg.  $\times 1$ .  
7. *H. burgeri*. Naturally deposited egg.  $\times 1$ .

(Figs. 1-5 drawn by Mr. Kuwabara, 6, 7, by Mr. Yatsu).

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Fig. 1.



Fig. 2.

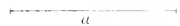


Fig. 3.



Fig. 4.



Fig. 5.



Fig. 7.



Fig. 6.





## Notes on Chimæra.

TWO JAPANESE SPECIES, *C. PILANTASMA* JORDAN AND SNYDER,  
AND *C. MITSUKURII* N. S., AND THEIR EGG CASES.

By

BASHFORD DEAN.

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*With 1 Plate.*

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Chimaeroid fishes enjoy the distinction of representing one of the largest (*i.e.*, major) groups of chordates of which least is known ; and they are forms, moreover, of especial interest, since they are often regarded as standing more nearly in the direct line of the higher vertebrates than even the oldest sharks. At the present day they are widely scattered, rarely common in any one locality, and they have proven unusually inaccessible to naturalists. Their embryology has not been described, and even their remarkable egg cases are known only in a few species.

From Japanese waters the only true Chimaera hitherto known is the one described, probably from the bay of Nagasaki, by Temminck and Schlegel, who figure it in their important *FAUNA JAPONICA* (1847). This species they here regard as identical with the common Chimaera of North Atlantic and Mediterranean waters.

*C. monstrosa*, a determination which has since been generally followed by both European and Japanese authors. Recently, however, Jordan and Snyder, studying the matter with greater care, have concluded that the Japanese species is distinct, and have given it the name of *C. phantasma*, describing it in the *Proceedings of the United States National Museum* for 1900, Vol. XXIII, pp. 338-339.

The latter authors distinguish it as follows:—*C. phantasma* "differs from *C. monstrosa*....having much longer pectoral fins and larger eyes." "Pectoral fin pointed;  $1\frac{2}{3}$  as long as the dorsal spine; when depressed its tip reaches middle of ventral." "Second dorsal fin a little higher than diameter of pupil; the posterior edge rounded; separated from caudal by a deep notch. Anal fin low, pointed posteriorly; separated from anal by a deep notch below the end of the dorsal. The lower caudal membrane extends posteriorly much farther than the upper."

Further than in the above notices the *Chimaeras* of Japan have received little attention.\* And I was therefore led to collect notes upon them during my stay at the Misaki zoological station, where the conditions were naturally favorable for my work, and where the Imperial University granted me the most generous privileges. To the University, and to the director of the station, Professor Mitsukuri, I am, accordingly, under deep obligation. I wish, also, in this connection, to express my sincere thanks to Prof. S. Watase, of the Imperial University of Tokyo, for his kindness in editing the present paper and in correcting the proof.

The present notes refer to the characters of *C. phantasma*, and include a description of a new species—*C. mitsukuri*, together with reference to the egg cases of both forms.

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\* *Chimaera ogilbyi*, an Australian species recently described by E. R. Waite (1899), is clearly distinct from Japanese forms. (*Mem. Australian Mus.* IV, pl. I, p. 48, pl. VI.)



**CHIMÆRA PHANTASMA.** *J. and S. (Pl. I, Fig. 3).*

This species is general in its distribution throughout the moderately deep water of the eastern coast of Japan, from the Hokkaido to Kyūshū. In the neighbourhood of Misaki, Sagami, where I have had an opportunity of examining living specimens, I find that it is taken in water of from 50 to 300 fathoms. Its distribution, however, like that of the Californian species, *C. collieri*, is peculiarly local. The fishermen will sometimes fish for days without obtaining specimens, and on the other hand on practically the same ground, they will sometimes obtain them to the number of twenty or more in a day. There are certain well-known portions of the reef "Outside Okinosé" where many specimens can usually be obtained. This species corresponds in point of size with *C. monstrosa* Linn. Female specimens measure 100 cm., or even more, in length; males are somewhat smaller, rarely exceeding 85 cm.

*Habits.*

The fish are usually sluggish in their movements when kept in shallow water. They swim about slowly, but oftener remain in the same position, merely balancing, moving their pectorals up and down, in slow rhythm. In confinement—*e.g.*, in shallow water, in large floating fish baskets—they rarely live longer than the second day. At their accustomed depth, on the other hand, judging from their behavior when freshly caught, I am convinced that these fish are normally very active, far stronger and more alert than I had been led to believe: for one is inclined to assume from their highly specialized dentition and poorly developed caudal fin that their movements are sluggish, similar to those of lophobranchs or teradonts.

*External Characters.*

This species presents a more compact and smoother appearance

than any chimaeroid which I have examined. (*C. collieri*, *monstrosa*, *affinis*, *mitsukurii*) in fresh condition ; and the general curvature of the head and body is roundly continuous to a degree which suggests a swift-swimming teleost. Living specimens are of exceptionally brilliant color and iridescence, altogether the most beautiful chimaeroids I have seen. The general color is silvery, and there is a series of jet black bands which pass down the side of the body from head to tail, fading away in the latter region. The bands are more numerous anteriorly where they frequently break into a series of mottlings, the lowermost following the lateral line. Between the anterior dorsal fin spine and the lateral line as many as four of these bands can be counted. The dark coloration continues along the roof of the head, and extends as far as the snout tip. The opercular fold shows also a degree of mottling as indicated in the accompanying figure. (Pl. I, Fig. 3.) The dorsal fin throughout its length is black at its base, but becomes unpigmented from this line outward as far as near the margin. Here there appears a continuous black band, narrow but distinct. The paired fins are pigmented notably on the anterior and posterior margins : their pigmentation ceases at the lobate bases of the pectoral fin (ventral side), but is continued irregularly on the ventral fins. I note also irregular pigmentation in the region of the ventro-median line posterior to the ventral fins and anterior to the rudiment of the anal.

The disposition of the mucous canal system of the head shows no noteworthy differences from other chimaeroids. The dental plates are stout and present well marked tritoral areas. In the "pre-maxillary" plates about eight tritoral lines are present, of which the median pair are most conspicuous. Each palatine plate is margined (laterad) by about a dozen grinding points and possesses two large tritors in the median region. The conspicuous tritor in the anterior

part of the plate is interpreted as the medianmost of the marginal series. In each maxillary plate about 26 tritors are present, far less distinct, however, than in the other plates. Of these tritors all but one are marginal, and in this row the most conspicuous are the third and fourth, counting from the symphyseal region and also the twentieth or thereabouts. The most conspicuous tritor of all is the one which occurs on the inner surface of the plate.

An examination of the viscera of this species has shown but unimportant differences from other chimæroids, *C. collieri* particularly

*Characters of the Egg Case.*

Two specimens of the egg case of this form are preserved in the Imperial University of Tokyo and two in Columbia University. The fifth specimen, referred to by Günther (*Ann. & Mag. Nat. Hist.* 4 (6.) 1889, p. 415), is probably preserved in the British Museum. Its general size and character are well shown in the accompanying illustration, Pl. I, Fig. 3. In point of size (length about 27 cm.) it is notably larger than those of other members of this genus. It approaches most closely to that of *C. monstrosa*, as figured, for example, by Grieg (1898, *Bergen's Museums Aarbog.* No. 3, p. 15.) I notice, however, that the web-like margin in the egg case of the Japanese species is much the narrower, and is lacking in conspicuous striation. On the other hand, the texture of the shell shows conspicuous longitudinal striae. In its form, too, the elongated narrow end of the egg case is proportionally narrower and shorter. The character of the opening end of the case is closely similar in both species, but the perforations occurring near the extreme tip of the narrow end of the egg case are finer and more numerous in the Japanese species. The color of the case when freshly deposited is a deep shade of Indian yellow. I have observed that two eggs are

deposited at a time, and that they are, for several hours at least, attached to the fish before they are deposited. During this time they hang freely into the water, attached only by the terminal of the narrow end.

Comparing this egg case in greater detail with those of *Chimaera collicii* and *C. monstrosa* (as shown in Grieg's figures), I find that the interlapping lamellae at the opening are about 46 in number, as opposed to 75 in *C. collicii*. The extent of these interlapping lamellae measure  $\frac{1}{16}$  the length of the entire case, as opposed to  $\frac{1}{5}$  in *C. collicii* and  $\frac{1}{9}$  in *C. monstrosa*. At the narrow end of the egg case the marginal perforations extend over somewhat more than  $\frac{1}{3}$  of the length of the egg case, as opposed to somewhat under  $\frac{1}{3}$  in *C. collicii* and  $\frac{1}{6}$  in *C. monstrosa*. Here 140 perforations are present as opposed to about 80 in *C. collicii* and about 70 in *C. monstrosa*. The narrow portion of the egg case (the marginal flaps not considered) measures about  $\frac{1}{6}$  the width of the widest region: the corresponding width in *C. collicii* is about  $\frac{1}{4}$  and *C. monstrosa*  $\frac{1}{5}$ . The marginal lappets are  $\frac{1}{2}$  the width of those in *C. collicii* and  $\frac{2}{3}$  those in *C. monstrosa*. The anterior end of the egg case, it may finally be noted, shows more distinctly than in other forms a lobe like dilation, and the marginal flaps in this region are distinctly directed towards the keeled face of the egg case. The keel in this species is proportionally lower than in the others.

### CHIMÆRA MITSUKURII, N. S. (*Pl. I, Fig. 1*).

Among the rarities in the zoological museum of the Imperial University of Tokyo, are the egg-cases \* of three different chimæroids. All were collected in the neighborhood of Misaki. One of them, with wide flap like margins, resembling the egg-case of *Callorhynchus*, has

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\* I wish to acknowledge with especial thanks the kindness of Professor Mitsukuri in placing them at my disposal for description.

since been associated by the writer with "*Harriotta*" *pacifica*; the second, of great length, was found to belong to *C. phantasma*; but the third egg-case remained unaccounted for. It showed clearly, however, that new species of *Chimera* was to be looked for on the Japanese coast; and it was further obvious that the species was notably smaller than the common one. For the egg-case (Pl. I, Fig. 2) was distinctly smaller, its measurements being 22 by 2.7 cm., as opposed to 27 by 3.5 cm. (*C. phantasma*). That the difference in these egg-cases is not one merely of size is at once seen in the smoother texture of the smaller egg-case, and by the different modeling of the apex of the larger end.

Accordingly I tried to collect the unknown species during my stay in Misaki; but my efforts met with no success, the fisher people not appearing to know of a smaller species of "gin samé," which they probably confused with immature specimens of *C. phantasma*. Just before the close of my stay, however, my search was rewarded: among a number of small specimens of *Chimera* brought me was an adult of a new species, which, as the possibility is not great of getting a second small species of *Chimera* in the same locality, readily answered as the parent form of the undetermined egg.

The specimen proved to be an adult male (Pl. I, Fig. 1) measuring 60 cm. in length, smaller, therefore, than the full-grown male of *Chimera phantasma* by about 25 cm. Its color was dark sepia below, blackish above, with here and there clouded lighter areas. A conspicuous feature is the greater relative size and strength of the dorsal spine: it projects beyond the tip of the succeeding fin rays, and shows serration, not only on its lateral borders, but on its anterior rim. The opisthure is of extraordinary length equalling  $\frac{1}{3}$  the length of the entire animal. In spite of this, the caudal fin itself is of relatively large size, as is also the continuous dorsal fin. The

unpaired fins are almost black in color, the tone softening somewhat near the body-wall. I note also that there is a distinct bluish tint on the anterior rim of the ventrals (which, by the way, are much larger than in *phantasma*) and along the somewhat adipose anal.

The mixipterygium is bifid, as in Gill's "*Hydrolagus*," although in other regards, *e. g.* long opisthure, the specimen is a typical *Chimaera*. The tip of the mixipterygium is covered with the usual fine shagreen, which in the present instance passes up around the crotch of the "clasper." The anterior ventral clasping organ is armed with five denticles. In visceral matters: there is an intestinal valve of  $3\frac{1}{2}$  turns: the lining membrane of the body cavity is unpigmented, while the wall of the gut is dark colored. The body wall is remarkably thin. Regarding dentition. "Premaxillary" plate is of large size, with fewer tritors, about eight, than in *C. phantasma*. "Maxillary" with three well marked tritors on its inner face, of these the most lateral the narrowest. "Mandibular" with a single tritor projecting sharply from its inner surface, much narrower than in the common species.

As nearly as I could ascertain, the present species was taken in deeper water off Misaki, more concretely, in water of about 300 fathoms. It belongs evidently to a somewhat deeper zone than the commoner species, which is taken oftenest in water of from 100 to 200 fathoms. That the new species is a deep water form is evident from the greater size of the eye,—which measures no less than  $\frac{1}{3}$  the distance from snout tip to the base of the dorsal spine,—from its dusky color, as well perhaps as from its greatly extended opisthure. I may note that it can be distinguished at a glance from the commoner species by the lack of the conspicuous longitudinal bands along its trunk region, by the large size of the ventral fins, and by a less distinct anal. The new species has been named in honor of Professor

Mitsukuri, the director of the Marine station at Misaki, as a slight testimony of my appreciation of his important and many-sided services to zoology. The type specimen is preserved in the Museum of the Imperial University of Tokyo. \*



\* A second example, an immature female, coming from the same locality, was afterwards found among the specimens of *Chimaera* in the University museum. As a juvenile specimen and discolored in alcohol, it had long been confused with the common species. This specimen was generously presented to Columbia University by the zoological department of the Imperial University.





BASHFORD DEAN.

**Notes on Chimæra.**

TWO JAPANESE SPECIES, *C. PHANTASMA* AND *C. MITSUKURI*,  
AND THEIR EGG CASES.

PLATE I.

## PLATE I.

### Japanese Chimaeroids and their eggs ( $\times \frac{3}{7}$ ).

Fig. 1 *Chimaera mitsukurii*, n. s.

2       "       "       "       "       Egg case.

3 *Chimaera phantasma*, Jordan and Snyder.

4       "       "       "       "       Egg case.

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## Notes on the Long-Snouted Chimaeroid of Japan, *Rhinochimæra* (Harriotta) *Pacifica*

(GARMAN) MITSUKURI.

By

BASHFORD DEAN.

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*With 2 Plates.*

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### Historical.

Harriotta described in 1894 by Goode and Bean, (*P. U. S. Nat. Mus. Vol. XVII*, pp. 471-473, Pl. XIX) added a third genus<sup>1)</sup> to the important but now greatly depleted group of Chimaeroid fishes. The new genus was created upon an examination of four specimens obtained by the "Albatross" in water of from about 700 to 1100 fathoms, between latitude 35° and 39° and longitude 70° and 74°. And the specimens are referred by their describers to a new species, *raleighana*. The largest specimen, a female, measured 64 cm. in length, a male 49 cm. and two "young individuals," 10 cm. or thereabouts in length. As

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1) To *Chimaera* and *Callorhynchus* Dr. Gill in 1862 (*P. Acad. Nat. Sci. Phila.* p. 331) suggested the addition of a genus *Hydrolagus*, on the ground of certain structural differences which he observed in *Chimaera colliei*, of the eastern Pacific. This form he distinguishes generically on account of its lacking a distinct anal fin, and of its possessing in the male a bifid instead of a trifid ventral clasping organ. I do not believe, however, that these differences can be accepted as of generic value, for in my studies upon this species I fail to confirm the observation as to the distinct character of the clasping organ in adult specimens, for this is sometimes trifid, and I find furthermore that there is considerable variation in the matter of the anal fin. The latter is adipose-like but varies to such a degree that one cannot draw a hard and fast line as to its presence or absence.

far as I am aware these are the only examples of the species extant.<sup>1)</sup> A second species of "Harriotta" was next described in 1895 by Professor Mitsukuri as *Harriotta pacifica*.<sup>2)</sup> Of this species, specimens have up to the present time been taken in the single region, that of Misaki, near the mouth of the bay of Tokyo, a locality which has become classic as the habitat of such rare and interesting fishes as *Chlamydoselachus* and *Mitsukurina*. As far as I am aware, all specimens of this Japanese species, save one, have been obtained in the fish market of Tokyo. Altogether seven individuals appear to have been preserved: three of these are now in the Imperial University of Tokyo, the fourth in the Museum of Comparative Zoology, Harvard University, the fifth in the Bohemian National Museum at Prague, the sixth in Columbia University, New York, and a seventh is now in the hands of Mr. Alan Owston, of Yokohama. The male specimen, which is apparently unique, was taken by the well known collector of the Misaki zoological station, Kuma Aoki. This is one of those in the Tokyo Museum.<sup>3)</sup>

In spite of the many interesting features which a surface study

1) A fifth specimen, a young male similar to the foregoing, has since been collected, and is preserved in the National Museum at Washington.

2) *Zool. Mag. Tokyo*. Vol. VII, No. 80, pp. 1-2.

3) The record of the specimens in Tokyo has been kindly forwarded me by Professor Mitsukuri. The first was obtained April 19, 1883, and was said to have been caught near Kurihama; the second, the male, was taken on May 9, 1898, by Kuma Aoki, on mitsu line, at a depth of about 400 fathoms, off the entrance of the bay of Tokyo, on the fisherman's ranges "Sengen-zuka gaké: Nago hitotsu:" the third, which was brought to the museum during Professor Mitsukuri's absence, 1898-99, has no definite label.

The present paper was prepared during my visit to Japan (1900-1901). Since then I have received from my friend Mr. Garman an important note, extr. from the *Proceedings of the New England Zoological Club*, Nov. 2d. 1901, Vol. II pp. 75-77, in which he regards the Japanese "Harriotta" as representing a new genus *Rhinochimaera*. Mr. Garman had had the privilege of comparing critically a type of *Harriotta raleighana* with a specimen of the Japanese form, and found marked differences in the character of the dental plates. I myself have since had the opportunity of examining in some detail the same type of *H. raleighana*, generously loaned me by the Smithsonian Institution, and I am able to confirm Garman's observation. Adopting the new generic name I have thought it best to allow the present paper to be published as it was written. I have changed my MS. therefore to read: "Harriotta" (in quotation marks) for the Japanese form.

of Harriotta at once suggested, from the standpoint of an understanding of the relationships of the Chimaeroid group, there are as yet recorded no observations upon the structural characters of this form, or even of its dental plates. Goode and Bean's description of *H. raleighana* was based upon purely superficial features, and the sanctity of the type specimens has hitherto precluded the National Museum from allowing an intimate knowledge of the genus to be obtained. I am accordingly under many obligations to my friend, Professor Mitsukuri, for the rare opportunity of examining in some detail one of the specimens of "*Harriotta*" *pacifica* of the Tokyo University. Among further kindnesses,—and I have to acknowledge many during my stay in Japan,—I am indebted to Dr. Mitsukuri for generously placing at my disposal his original drawings of this chimaeroid (Cf. Pl. I, Figs. 2–3), and furthering my work at the laboratory in every way in his power. And in publishing the present paper I should not fail to express my sincere thanks to Prof. Watasé, of the Imperial University, for his cares in editing the MS. and in correcting my proof—favors which an author far distant especially appreciates.

By a long way the most interesting feature which "*Harriotta*" presents, at least in the single adult specimen examined, is the distinctness of its palato-quadrate cartilage.<sup>1)</sup> This can be clearly outlined on both sides of the skull,<sup>2)</sup> and appears to be the only case in which this important morphological suture has been observed in any adult chimaeroid. It may be noted that the embryo of *Chimara collicii* presents a somewhat similar appearance. On the other hand, my observations on "*H.*" *pacifica* have convinced me that this chimaeroid is

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1) In Chimaeroids this element cannot be identified in the mature skull, it having fused completely with the sides of the cranium, producing the well known "holocephalous" skull. But in the specimen of "*Harriotta*" the dorsal sutural joint is still retained, enabling the outline of this element to be clearly followed.

2) Sad to relate, this feature is probably exceptional! *Vide infra*.

not as widely distinct from the other genera as I had been led to believe from the work of Goode and Bean,—always granting that the species *raleighana* and *pacifica* belong to the same genus, and of this we cannot be sure until there can be had a better knowledge of the specimens in Washington. I thus find that “clasp ing organs” are present in “*Harriotta*” *pacifica*, very much as in other Chimaeroids, and we are led to infer that the male specimen (49 cm.) of *H. raleighana* was distinctly immature. But upon this again we cannot decide until there has been a more critical examination of the type specimens.

The notes I have collected regarding the Japanese “*Harriotta*” are arranged as follows :

- I External Characters.
- II Integument.
- III Skeleton (including fin structures).
- IV Viscera.
  - a. Gills.
  - b. Circulatory.
  - c. Digestive tract and appendages.
  - d. Urogenital.
- V Characters of the egg-case.
- VI General Considerations.

I. **External Characters.** Pl. I, Figs. 1, 2, 3 and 8.

A mature specimen of a female “*Harriotta*” *pacifica* measures about 120 cm. in length, and of a male about 90 cm. The specimen which I dissected, a full grown female, measured over 130 cm.

In outward appearance, “*Harriotta*” suggests more closely *Calorhynchus* than *Chimaera*. It has thus the broad, somewhat heterocercal tail, a greatly produced snout, and fewer dermal denticles. As in most chimaeroids, a distinct opisthure is present. The color in this



species cannot be accurately determined, since all specimens have been discolored in alcohol. The general tone of the trunk, however, seems to have been plumbeous, darker above than below. The muzzle is white, and this color extends forward along the sides and ventral margin of the greatly produced snout. No definite markings are present. In the specimens examined the sides of the trunk show many transverse foldings which I have not observed in similarly preserved specimens of *Chimaera*, and they are probably to be interpreted as symptoms of abyssal living. The dorsal fins are margined with a dusky band, and the paired fins are darkest along their anterior margin. The dorsal spine differs little from that in the other genera; if anything, it is somewhat more delicate, and I cannot confirm in "*H.*" *pacifica* at least the presence of the "broad triangular spine" which Goode and Bean have laid stress upon in their definition of the genus. I noticed in one Japanese specimen, the best preserved, in fact, that the floor of the sensory canals is in many places black, a condition which seemed at first due to the presence of foreign matter. Closer examination, however, showed that this was normal pigmentation, and traces of it were afterward found in other specimens.

The clasping organ (mixipterygium) of the male is indicated in Pl. I, Fig. 8 (its tip at *c*): it is essentially similar to that in *Callorhynchus*. Near the antero-proximal rim of the ventral fin occurs the usual protractile organ at Fig. 8 *a* (its tip at *b*); it preserves 4 anterior marginal denticles and the same number occurs on its fellow. Its sharply truncated lobate end distinguishes it from the similar structure in *Chimaera*. The mixipterygium is remarkably long and slender, its supports combining to form a single element. Its distal end is enlarged, globular, and is furnished with dermal denticles, as shown in the Fig. 8. The frontal clasper, 8 *d*, differs little from that of other recent chimaeroids; its dermal denticles, however, are fewer (but

55 were counted) and smaller. Incidentally, the sheath of the frontal organ is longer, and from the great length of the socket-like depressions, which form sheaths for the superjacent denticles, one can reasonably conclude that the snout of "Harriotta" was capable of considerable vertical movement.

From our present knowledge *H. raleighana* and "*H.*" *pacifica* differ from one another in the following regards :

*H. raleighana* Goode and Bean.

Head length, measured from in front of gill opening, constitutes one fourth that of entire animal. Snout tapers somewhat suddenly. Paired fins broad at bases thence narrow acutely. Second dorsal fin low, with margin nearly straight. Dorsal lobe of caudal fin with well marked dermal rays. Series of conspicuous dermal tubercles situated along the dorsal region of the trunk, near the unpaired fin.

"*H.*" *pacifica* Mitsukuri.

Head length about two sevenths that of entire animal. Snout tapers gradually, *i.e.*, in very acute angle. Paired fins narrow and long. Second dorsal fin high, with margin rounded. Dorsal lobe of caudal fin fleshy with indistinct dermal rays. Dermal denticles along dorsal margin of caudal fin, but absent on the trunk. In addition to these characters the present species has thin, flat tritorless dental plates, produced ectad so as to form a sectorial mouth-rim. Also an undivided mixipterygium. The corresponding features in *raleighana* have not as yet been described.<sup>1)</sup>

## II. Integument.

The only dermal denticles observed in the female specimen are scattered along the dorsal rim of the caudal fin. Over fifty of these were counted, situated at irregular intervals (about 3–5 mm.) apart.

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1) Cf., however, Garman's recent paper, *op. cit.*

They are located usually in pairs and together straddle the rim of the fin, causing this in profile to appear somewhat serrate. The denticles themselves are somewhat tumid, imperfectly calcified.

In the male dermal denticles occur in the customary positions: *i.e.*, on the frontal and on the two ventral pairs of clasping organs. The condition of the frontal clasping spine is illustrated in Pl. I, Fig. 8 *d*. The antero-ventral pair of clasping organs is shown in the same plate, Fig. 8 *a, b*, and of these the stout recurved marginal denticles differ little from those in *Chimaera*. The denticles on the mixipterygium are also essentially similar to those of the other genera. In connection with the mucous canal system, however, I fail to find in "*Harriotta*" the distinct dermal supporting plates well known in *Chimaera*. We thus find that the mucous canals of the suborbital region are not provided with prominent and almost plate-like supports: one infers, however, that these supports are present in a reduced form after drawing a needle sharply along the floor of a canal. It is observed that in "*Harriotta*" the mucous canals, although distinctly of the chimaeroid pattern, do not open widely to the surface, as in the case of many bathybial forms. So closely are the opposing margins drawn together<sup>1)</sup> in this type that the point of a common needle can hardly be drawn through the canal without causing its margins to separate. In the disposition of the sensory canals, "*Harriotta*" approaches more closely *Callorhynchus* than *Chimaera*.

### III. Skeleton. Pl. I, Figs. 4, 4*a*, 5, 6, 6*a*, 7.

The skull, as has already been noted, retains a well-marked line showing where the palato-quadrato is completing its fusion with the skull. It may be noted that this distinctness of the palato-quadrato

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1) This condition can hardly be due to artifact since it does not occur in the case of the allied forms, *Callorhynchus* or *Chimaera*, when similarly preserved.

element, unique in an adult chimaeroid, appears on both sides of the specimen dissected.<sup>1)</sup> If we accept this important character as a normal one it is remarkable that the skull differs in further regards so little from the well known conditions in the other Chimaeroids. For, if we except the great size and shape of the upper median (rostral) cartilage there remains little to distinguish "Harriotta" from *Callo-rhynchus*. The contour of the cranium is closely similar, as is also the proportional size of the orbits, and the position of the foramina of the nerves. Referring again to the palato-quadrate element I note that this is most distinctly marked out at its hinder border, as indicated in the figure. I found however by slicing the cartilage in this region that the separateness of the element is in a measure deceptive, for it is superficial only. On the other hand, in the region of the anterior rim of the orbit the line of suture can be followed deeply into the cartilage. The striking feature in the mouth of this form is in the beak like development of the dental plates, in this regard quite unlike any Chimaeroid described, for the plates themselves are reduced to an almost horn like texture, losing the calcified tritoral points, so characteristic of the entire group. And their edges are sectorial, narrowing away beak fashion from their surface of origin. The appearance of the mandibular plates is given in Figs. 6, 6a. The "maxillary" plates are proportioned larger and narrower than in other recent chimaeroids, over three times as long as wide; and there is thus a narrower band of pulp from which the plate takes its origin. The "pre-maxillary" plates are also constricted: instead of becoming opposed to one another in

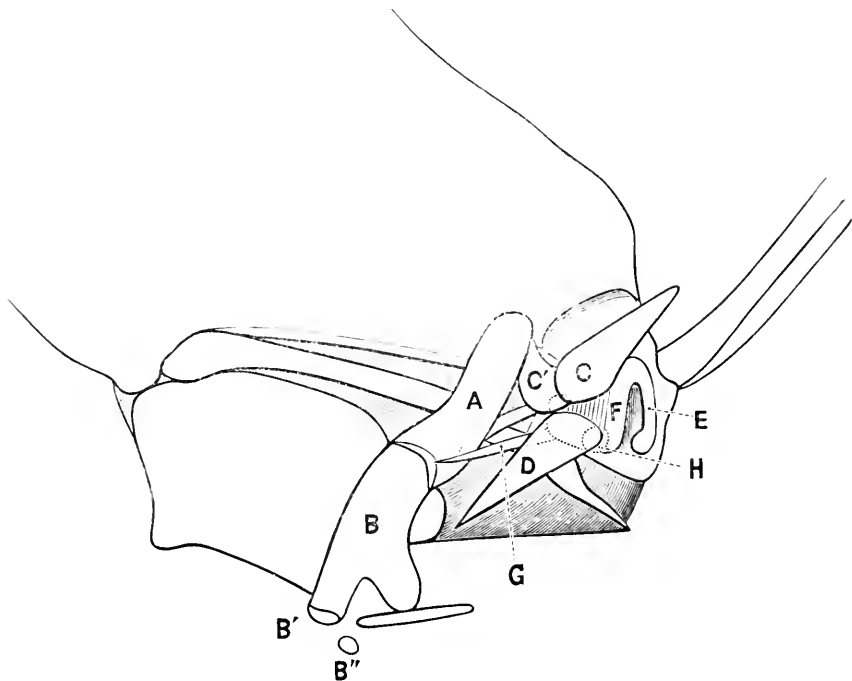
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1) In the specimen in the museum of Columbia University, which I have had the opportunity of examining since the above was written, no trace of this suture occurs on either side! Accordingly, in the absence of further data, I am led to believe that the sutural condition in the former specimen is exceptional. For, upon examination of a series of preparations of the sutural region on *Chimera collieri*, I have found in a single specimen, nearly full grown, a male, that a distinct line of union is indicated. In this instance, however, the line is not as distinct as in the above described specimen.

an almost transverse plane, as in *Chimaera*, for example, they meet in an acute angle, their free edges continuing the long cutting plane of the "maxillary" plates. (Plate I, Fig. 5).

In the region of the snout the unpaired (rostral) cartilage is of extraordinary size. It measures one and one half times the length of the entire cranium. It is stout, narrow, and somewhat spatulate: at its proximal end, where it is securely attached to the cranium, there is a (movable) joint. The shorter, more anterior supporting element of the snout is one of a pair, its fellow arising close beside it, as is shown in the figure.

The more prominent relations of the complex labial and related cartilages are indicated in Text-fig. 1, the elements having been



Text-Fig. 1. Diagram showing lateral aspect of mouth cartilages of  
*"Harriotta" pacifica*.

denoted by letters, since they have not as yet been compared satisfactorily with those of other chimaeroids. The cartilages are connected with the skin by fascia: their other attachments are as follows:

*Attachment.*

*Element.*

*A* Attached to anterior dorsal as well as to caudal arm of the element *C*., articulating to *B*., and posteriorly to the skin and skull by muscles.

*B* With *A* strengthens the integumental fold forming the outer angle of the mouth. From an antero-ventral eminence this plate supports a loose fold of the margin of the lip. This eminence forms also in part the posterior support for the broad under lip, which depends notably from the jaw. *B'* and *B''* are small elements closely related to the ligaments attached to the ventro-posterior arm of *B*.

*C* Connected by ligaments with the anterior projecting pair of cartilages, forming in connection with the latter a mechanism which raises or depresses the whole labial apparatus. Connected ventro-mesad with the dorsal rim of the folding pair of cartilages *E-F*; ecto-distad, by muscle and ligament, to *D*; attached, also, along extended hinder (caudad) rim, mainly ectal, to *A*. Its hinder arm, the element *C'*, attached proximad to skull by strong ligament (near and dorsal to the posterior nasal opening).

*D* Connected anteriorly with *C*. Its posterior arm, enveloped in a loose marginal fold of the skin, passes outside the angle of the mouth.

*E, F* *E* and *F* together (with hinge joint) form the rim of the nasal opening, a movable arm constituting the septum

between the anterior and posterior navial openings. *E* is attached strongly to skull by ligaments in the region immediately above the "premaxillary" dental plates. Also to *C*, as above noted. The septum is moved notably by means of the element *G* attached to its posterior eminence.

*G*        Connected by ligament to the element *F* and to the joint *A-C* : by fascia to *B*.

*H*        A small element attached to the side of *F*. In this region other small elements are to be noted, connected with nasal flap on the one hand and with the upper lip on the other.

In the structure of the cartilaginous gill arches "Harriotta" again resembles closely *Callorhynchus*. These elements are figured in lateral and in ventral aspects in Pl. I., Figs. 4 and 7. The suspensorium consists of the usual chimaeroid elements, a stout ceratohyal, a greatly reduced hyomandibular terminating in a small element to which in other chimaeroids various homologies have been ascribed. This element may be regarded provisionally, *i.e.*, until its development is known, as the serial homologue of a pharyngobranchial. Accepting this determination it will be seen that the reduced hyomandibular is coming to establish an articular relation directly with the cranium, a character of considerable importance in vertebrate morphology. Of the remaining five arches the first two are complete, possessing hypobasibranchial, ceratobranchial, epibranchial and pharyngobranchial elements. The third true gill arch possesses but hypobranchial and ceratobranchial elements, its pharyngobranchial segment occurring in common with that of the fourth gill arch. In the latter arch, what appears to be the somewhat displaced hypobranchial segment probably represents a fusion with the hypobranchial element

of the fifth arch as well. The fifth arch, rudimentary, exhibits a cerato-branchial, and a greatly reduced pharyngobranchial in the shape of a discrete tubercle of cartilage attached to its dorsal terminal. The unpaired median series of ventral cartilages is poorly represented. A basihyal is closely moulded to a stout hypobranchial, and this alone of the median elements is directly articulated with an arch. It is stoutly attached to the ceratohyal. I note also a pisiform cartilage which is attached by ligament to the hypobranchial of the third gill. The posterior median element is a stout ensiform plate attached by a broad ligament to the common hypobranchial of the fourth (and fifth ?) arch and to the ceratohyal of the fifth arch.

#### *Vertebral Column.*

As in other chimaeroids, the notochord is strengthened by calcified rings occurring within the notochordal sheath. Neural and haemal arches, however, are represented throughout the anterior three-quarters of the column. In the region of the anterior half of the column there are neural and interneural cartilages. On the ventral side of the chorda, appear haemal plates more or less irregular in size, and often exhibiting fusion. These characters are well shown in Pl. I., Fig. 4. In the block-like portion of the column which immediately follows the skull a number of foramina are present for the dorsal and ventral nerve-roots. The openings, representing about twelve nerves, are obviously crowded together and afford conclusive evidence that a considerable shortening of the column has taken place, especially in the more anterior region.<sup>1)</sup> Furthermore, according to the relations of the posterior portion of this plate to the adjacent neural and interneural plates, one can, I believe, safely infer that the dorsal expansion of this compound element is equivalent to

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1) Similar conditions occur in *C. collieri*.



the fused neural plates of the original segments whose presence is attested by the distinct openings for the exit of spinal nerves. This great expansion of the neural elements has probably been concomitant with the evolution of an erectile dorsal fin which required a firm hinge for its anterior spine. The disposition of the muscles which erect and depress the fin bespeak a thinning away of the median portion of this neural plate, and the thickening of its anterior margin. Further examination of this portion of the column gives no evidence that discrete centra, in the elasmobranchian sense, are represented. The cartilage which encases the sides of the notochord can in this form best be interpreted as coalescence of the neural and haemal cartilages, a coalescence apparently the result of a specialization of structures for supporting and operating the dorsal fin.

*Unpaired Fins.* Pl. I, Fig. 4.

The series of dorsal fins is more clearly marked than in *Chimaera*. The first dorsal fin is separated from the second by a low, extended and rayless fold of integument. The second dorsal, which presents a rounded upper margin, bears a series of close-set dermal rays. This again is separated by a considerable interval from the dorsal lobe of the caudal fin. In this lobe, which is somewhat adipose, dermal rays are present, but are inconspicuous. The first dorsal fin possesses the basal support usual in chimaeroids. Its dermal rays are drawn together into about half a dozen strong supporting elements of the fin web, as shown in the figure. The anterior spine is slender and remarkably delicate; its tip, in fact, is broken off in all but two of the specimens examined. And it is in the tip, only, *i. e.*, in the upper third of the spine, that a postero-lateral marginal serration occurs. The "denticles" are here minute and disposed somewhat irregularly. The surface of the spine is ornamented with a few

indistinct ridges, which are arranged in a somewhat wavy pattern near the base of the spine.

The cartilaginous basal supports of the dorsal are about seventy in number : they are similar in shape but are graded somewhat in size, the foremost and hindmost being the smallest. The first element in this series is inclined forward and is the only one in this position. A similar series of cartilaginous elements support the dorsal lobe of the caudal fin : of these first two are small and separate, but the next set, thirty odd in number, follow in a graded series, compact, with tips and bases apposed. Further caudad still the supporting elements string along loosely, like neural spines.

There is no anal fin. The ventral lobe of the caudal, however, is of considerable size, and is closely set with dermal rays. Its basal supports are first evident in a position much further caudal than one would expect from the disposition of the dermal rays, and they are altogether smaller and more delicate than one would naturally expect from the size of the web of the fin. The first two elements of the row are inconspicuous and—as an individual variation perhaps—are situated at a considerable distance from the column ; the remainder, although close to the column, are not firmly connected with it. One need hardly add that in the urostyle no traces of haemal or neural elements can be determined.

*Paired Fins and Girdles.* Pl. I, Fig. 4.

The cartilaginous supports of the pectoral fin occupy a great extent of its entire surface, greater in proportion than in the case of other chimaeroids. And the fin is in general a narrower one. About the usual number of radialis are present, twenty-six rows in this specimen, having the usual relations to basalis. A thick distal row of cartilages, representing the terminal segments of corresponding

radalia, is prominently marked off on the preaxial region of the fin, a structural difference from other chimaeroids, correlated doubtless with a greater degree of movement of the anterior rim of the fin. It is to be noted that the element best known as mesopterygial has attained considerable physiological importance, functioning as a kind of "humerus" for the fin. It is a stout narrow plate possessing considerable mobility, both at its juncture with the shoulder girdle and with the pro- and metapterygial elements. The shoulder girdle is strong, even for a chimaeroid, especially in its ventral moiety.

The ventral fin is notably narrowed — *i.e.*, antero-posteriorly. Basalia, greatly constricted, are represented in a single oblong plate, with which fuse also the two most anterior radials. The anterior margin of the supporting lobe of the fin is formed, is in the pectoral fin, by an encircling row of stout cartilages, which doubtless represent the distal segments of the anterior radials. The most anterior element of this row of supports is an elongated cartilage which may represent either the distal end of the first radial, or, more probably, a union of this element with a still more anterior cartilage. In the present example twelve distinct radials are counted. Posterior to the fin proper, and loosely attached by ligament to the plate of fused basals appears a rudiment of the mixipterygium of the male. This structure, now noted for the first time in a chimaeroid,\* is seen to consist of two short and delicate segments. A further peculiarity of the pelvic fin is the greatly reduced size of its articulation to the girdle. The girdle itself is small, thin and delicate. Its upper blade

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\* The rudimentary "clasping organ" is so well known in female sharks that the present writer was led to represent it in such a condition in his "Fishes Living and Fossil." Unfortunately he did not think it necessary at the time to insert the word "rudimentary" in the brief explanation attached to this figure, and he has therefore caused Dr. C. F. Jungerson to believe that it was his intention to append a functional "clasping organ" to a female shark! Jungerson's misunderstanding would not have occurred had he taken the pains to consult the text which accompanied the figure.

terminates in a posteriorly curved process which is doubtless the serial homologue of the dorsal terminal of the shoulder girdle. The ventral blade of the girdle bends ventro-mesad and come to lie in an almost horizontal planes.

#### IV. Viscera.

##### *A. Gills.*

As in other chimaeroids an opercular fold arises from the posterior margin of the first ceratohyal, is strengthened by a series of parallel cartilaginous rods, and encloses completely the excurrent openings of the gill. An interesting feature however in the present form is that the outer margins of the supporting tissue of the remaining gill bars fuse together ectad, both dorsally and ventrally, and together form a series of grooves which pass outward and fade away near the external opening of the opercular fold. In the opercular gill the vascular lamellae extend outward from the gill bar halfway to the free margin of the fold, following closely the parallel cartilaginous rays which strengthen it. In the remaining gills the median supporting septa extend no further outward than the tips of the vascular lamellae, a condition, however, which does not, of course, apply to the extension of the supporting septa at their dorsal and ventral ends, as already noted. Four gill slits are present, the fifth having been suppressed. There is no trace of a spiracle. The number of lamellae in the gills averages fifty : they are slightly less numerous in the opercular gill, and in the hindmost hemibranch about forty-five are present. It is interesting to note that the gill lamellae are continued around the dorsal margins of the gill slits, and that traces of them can be found around the ventral margins. Gill rakers are present, but they are small, fleshy and widely separate from one another, to be interpreted therefore, as rudimentary organs.

In the different rows they vary from four to ten, eight being about the average number.

*B. Circulatory.* Pl. II, Figs. 9 and 11.

The branches of the dorsal aorta are stouter than in specimens of *Chimaera* of a similar size. And the length of the branches supplying the digestive tract is notably greater. The conus arteriosus presents two rows of valves, approximately equal in size. Four valves are present in the anterior row, and three in the posterior. In addition to these, several rudimentary valves are situated in the folds of the conus near its opening into the heart.

*C. Digestive Tract and Appendages.* Pl. II, Fig. 9.

The gut is narrower in calibre and proportionally longer than in other Chimaeroids examined. The spiral valve completes four turns. The liver is bilobed, and is somewhat smaller than in *Chimaera*. If one recalls the sectorial dental plates in this form and the absence of tritoral areas it is interesting to find that the gut contained debris of small fishes, and was altogether lacking in the remains of hard shelled forms, crustacean or molluscan.

*D. Urogenital System.* Pl. II, Figs. 9 and 10.

The oviducts differ little from those of *Chimaera*. They are more conspicuous in that they lie unpigmented (*ord.*) against the black dorsal wall of the body cavity. Minor differences include the shape of the capsular gland which in surface view presents a Y-shaped appearance on account of the mode of grouping of its lamellae. In the specimen dissected, a single external opening was present for both oviducts (*u.g.*). I am, however, inclined to regard this as a condition of artifact, since I have seen a somewhat similar appearance in polyor

preserved specimens of *Chimaera*. In Pl. II, Fig. 10, the lower apertures are seen to be marked by tumid eminences (*o.l.o.*) lying just within the opening above referred to. In the same figure there is a well defined central area (*c.*) in which is moulded the rounded egg-containing portion of the case; also at the sides a wide flat tract (*m.*) in which the lateral flaps of the egg-case are formed. In the crease at the outer margin of this area there happened to be present in the specimen a small portion of the lateral flap of an egg-case here worthy of mention since it afterward proved of value in identifying a separately collected egg-case of this form. Both right and left ovaries were present in the specimen, though only one of them has been figured. In size and position they correspond to *Chimaera*. The kidney is apparently a less conspicuous organ than in *Chimaera*; it is greatly flattened relatively, and is entirely concealed by the pigmented peritoneum. The urinal papilla is similar to that of *Chimaera*.

#### V. The Egg-Case. Pl. II, Figs. 12, 12a, 12b.

Two egg-cases of an undetermined chimaeroid are preserved in the collection of the Imperial University of Tokyo, and a similar one, but less perfect, I was able to secure for Columbia University, through a local collector. The locality in which these egg cases were obtained corresponds to that of "*Harriotta*" *pacifica*, and, by an examination of the oviducts in this form and by a comparison of a portion of an egg-case taken from the oviduct, I find that the problematical specimens can be referred to "*Hariotta*" with reasonable certainty.

From an examination of the specimens preserved in Tokyo, which, by the way, are alcoholic and quite well preserved, one is at first given the impression that the eggs belong to *Callorhynchus*: there is the same broad lateral flange and the same general shape of

the egg-surrounding part. As *Callorhynchus*, however, is not known to occur in Japanese waters, and as closer study brings out distinct differences in these egg-cases, one would naturally refer them to "*Harriotta*," even if a fragment of the undoubted egg of this form had not been discovered. The egg-case, Pl. II., Fig. 12, is of extraordinary size, measuring over 26 cm. in length. A dried specimen measures 16.5 cm. The median portion of the capsule resembles that of *Chimaera*, save in the greater proportional length of its wider, or exit-end. On the longer, narrower end, however, no keel-like ridge is present. At the immediate sides of the narrow end (Fig. 12*a*) the apertures for ingress of water are restricted to a shorter space, but, apparently in compensation, are produced further lateral: they do not pass through to the opposite side. The exit-end of the egg-case (Fig. 12*b*) is furnished with a series of interllapping lamellae somewhat as in *Chimaera*, but they are restricted to a shorter space. I notice also in an egg-case which bears evidence of having been long deposited, a large mass of horny fibres closely felted together, concealing this region of the egg. These fibres arise both from the outer margins of the opercular-like folds, as well as from the egg surface lying between them. The lateral flaps of the egg-case recall of *Callorhynchus*: they are strengthened by sixty or more thickened and folded ribs, and the marginal line is smooth and delicate. In texture, shape and color the entire case resembles strikingly a "branch" of a heavy fucoid alga.

## VI. General Considerations.

At the time of its original description, *Harriotta* was said to possess "no cephalic organ," and that its claspers were "small and simple." From these characters, unique among chimaeroids, a reader was naturally led to expect that the new type might prove of value as

a key to the relationships of its group. An examination of allied Pacific species, however, demonstrates, as we have seen, that such expectations are not to be realized, and that this form of Chimaeroid is to be looked upon as of no greater value than the better known genera. Even its skull structure is not convincingly primitive, for certainly little stress can be laid upon the distinctness of the palato-quadrato suture in one specimen when it is altogether lacking in a second one. In some regards, on the contrary, this chimaeroid is even furthest away from our conception of the ancient form, *e.g.* in its highly specialized rostral and labial cartilages, its greatly produced enant and tritorless dental plates,\* its coalesced gill supporting elements, its compressed paired fins, its more perfectly obliterated mesenteries. And so far from possessing no well marked clasping organs, it has them in a condition of high specialization; thus in the case of the mixipterygium I have evidence that three supporting elements of the other chimaeroids are present, but have undergone a process of coalescence, to the degree of producing a narrow and delicate appendage, bulbous at the tip, and provided with fewer and larger denticles than in other forms. Moreover, as there is reason to believe that this type of chimaeroid is from deeper water than the other members of the group, we can hardly expect that its further study will yield convincing data as to its primitiveness. In its egg-case it is as highly specialized as *Callorhynchus*.

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\* From Garman's preliminary note he is evidently of the opinion that the tritorless condition is primitive in the dental plates of chimaeroids. This rather startling view;—for without further explanation, it implies that the dental plates are not to be derived from elasmobranchian (conditions,—is based upon two untenable premises: (1), resemblance to the dental plates of Cretaceous or Jurassic myriacanth, and (2), similarity to the very early conditions of the teeth of other living Chimaeroids. The first of these premises is, I am convinced, based upon a misconception of the dental characters of *Myriacanthus*, in which many tritoral areas are present; the second upon an interesting larvalism which the young plates present, growth occurring precociously at one rim of the plate. From my study of the development of *Chimaera coliei* I am led to believe that the dental plates of *Rhinochimaera* persist in a larval condition: they have never passed through the stage represented in Harriotta, and the two forms are thus more than generically distinct. The latter genus is, therefore, to be removed from the *Rhinochimaeridae*, and becomes the type of a new family—*Harriottidae*. Upon *Harriotta* the writer has in preparation a separate paper.



BASHFORD DEAN.

Notes on the Long-Snouted Chimaeroid of Japan,  
*RHINOCHIMAERA PACIFICA.*

PLATE I.

## PLATE I.

"*Harriotta*" *Pacifica*, Mitsukuri. Superficial characters and skeleton.

- Fig.** 1 Lateral view of adult female X about  $\frac{5}{13}$   
2 Dorsal view of head of same specimen.  
3 Ventral " " " " " "  
4 Skeleton of same specimen.  
4 a Ventral view of pelvic girdle.  
6, 6 a Mandible, ventral and dorsal (visceral) aspects.  
7 Visceral arches, ventral aspect.  
8 Ventral fins and mixipterygia of male. X about  $\frac{1}{2}$   
8 a Antero-lateral clasp ing organ, ventral aspect. X about 1.  
8 b Antero-lateral clasp ing organ, view of tip. X about 1.  
8 c Tip of mixipterygium.  
8 d Frontal clasp ing organ. Slightly reduced.
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*Pteranodon longirostris* (Morse)



BASHFORD DEAN.

Notes on the Long-Snouted Chimaeroid of Japan,  
*RHINOCHIMAERA (HARRIOTTA) PACIFICA.*

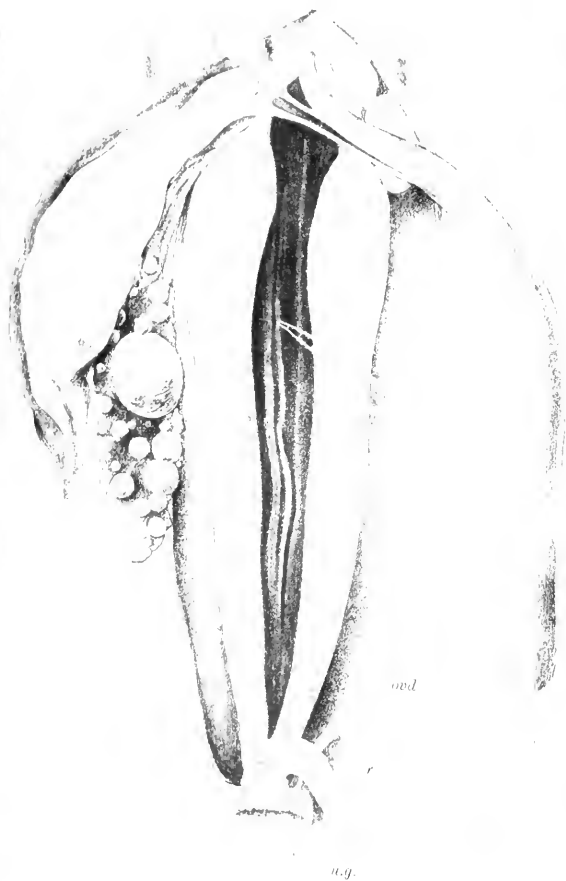
PLATE II.

## PLATE II.

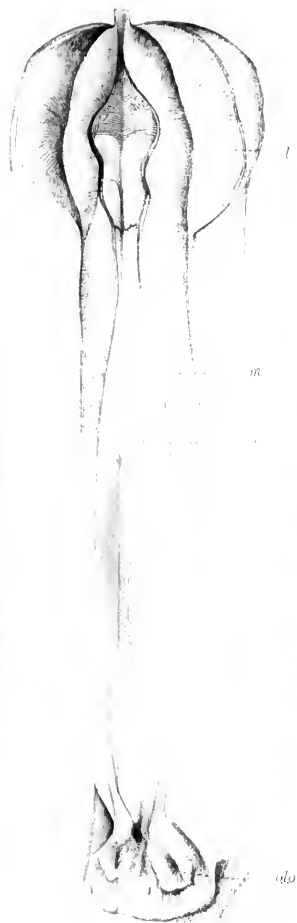
"*Hariotta*" *pacifica*, Mitsukuri. Viscera and Egg case.

- Fig. 9 Body cavity opened, exposing liver, gall-bladder and duct, right ovary (left has been removed), alimentary canal with mesenteric vessels, and oviducts (*ovd.*). Urogenital opening is indicated at *ug.* and rectum at *r.*
- 10 Oviduct, right, laid open. *c.* Central portion of capsular region. *l.* Capsular gland, showing closely arranged lamellae. *m.* Marginal portion of capsular region. *o.l.o.* Opening of left oviduct.
- 11 Conus arteriosus, laid open, exposing rows of valves. X about 5.
- 12 Egg capsule. X about  $\frac{5}{8}$ . Oka del.
- 12 a Detail of posterior end of egg capsule (dorsal aspect) showing ventilating apertures.
- 12 b Detail of anterior end of egg capsule (dorsal aspect), showing mode of opening, the lamellae of the left side having been separated. (This side corresponds to the keeled side of the egg case in *Chimaera*).
-

Fig. 9



10



12



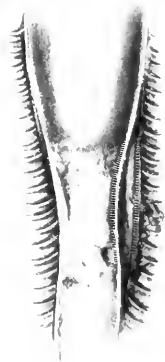
11



12a



12b







## Ueber die im Bereiche der rationalen complexen Zahlen Abel'schen Zahlkörper.

Von

T. Takagi,

a. o. Professor der Mathematik an der Universität zu Tōkyō.

Kronecker hat zuerst den Satz ausgesprochen, dass alle im natürlichen Rationalitätsbereich Abel'schen Zahlkörper durch die Kreiskörper, d.h., die aus den Kreisteilungsgleichungen entspringenden Zahlkörper erschöpft sind. Der erste vollständige Beweis dieses schönen Satzes rührt von H. Weber<sup>1)</sup> her, welchem sich in neuester Zeit ein einfacherer und direkterer Beweis von Hilbert<sup>2)</sup> zugesellte. Es war auch Kronecker, der der Vermutung Ausdruck gab, dass alle in Bezug auf einem imaginären quadratischen Zahlkörper relativ-Abel'schen Zahlkörper durch diejenigen Körper erschöpft seien, welche aus den Transformationsgleichungen der elliptischen Functionen mit singulären Moduln entstehen. So wahrscheinlich auch diese Vermutung durch die Untersuchungen von H. Weber, Hilbert, u. A. geworden ist, harret die Frage doch noch der entscheidenden Erledigung. Indessen es gibt specielle Fälle dieser grossen Aufgabe, wo man von vorn herein eines glücklichen Abschlusses sicher sein

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1) H. Weber, *Acta Mathematica*, Bd. 8; *Lehrbuch der Algebra*, Bd. II.

2) Hilbert, *Göttinger Nachrichten*, 1896; *Jahresbericht der Deutschen Mathematiker-Vereinigung* IV.

kann, nämlich die, wo die zu Grunde gelegten quadratischen Körper einclassig sind, also z.B. durch die dritten und die vierten imaginären Einheitswurzeln erzeugt werden; sie bilden in der Tat die unmittelbare Verallgemeinerung des Satzes über die Kreiskörper. Der zuletzt genannte specielle Fall, welcher sich auf die Teilung des Umfangs einer Lemniskate bezieht, und von jeher besonders hohes Interesse beanspruchte, wird nun in den folgenden Zeilen behandelt, und die Bestätigung der Kronecker'schen Vermutung in diesem speciellen Falle wird unter Benutzung der Hilbert'schen Methode<sup>1)</sup> bis zu den Einzelheiten ausgeführt.

Diese fast überflüssigen Einleitungsworte schliesse ich mit dem Ausdruck herzlichsten Dankes an den Herrn Prof. Hilbert in Göttingen, dessen Anregung diese Erstlingsarbeit ihr Entstehen verdankt.

### §. 1.

Für die  $\wp$ -Function mit dem Periodenverhältnis  $i$  ist  $g_3=0$ ; nimmt man  $e_1=1$ ,  $e_2=-1$ ,  $e_3=0$ , so wird  $2\omega=\Omega$  reell,  $2\omega'=\Omega i$  rein imaginär;  $\wp(u)$  ist reell für reelles  $u$ , und nimmt conjugirt complexe Werte an für conjugirt complexe Werte des Arguments. Es ist ferner  $\wp(iu)=-\wp(u)$ . Zwischen dieser  $\wp$  Function und der Function  $sn\,u$  mit  $K=i$  besteht die Beziehung

$$\wp u = (sn\,u)^{-2}$$

mit demselben Argument für die beiden Functionen; ferner

$$2K=\Omega, \quad 2K'i=(1+i)\Omega$$

$$sn\,iu=i\,sn\,u$$

---

1) Hilbert, *l. c.*

Verstehen wir unter  $\mu$  eine ganze Zahl des Körpers der rationalen complexen Zahlen, welchen wir im folgenden stets mit  $k(i)$  bezeichnen wollen, so gelten für diese Functionen die folgenden Multiplicationsgesetze:

I.  $\mu$  ist eine ungerade ganze rationale primäre Zahl in  $k(i)$ :

$$sn \mu u = x \frac{\zeta_\mu(x^4)}{\zeta_\mu(x^4)} : \quad x = sn u$$

$$\wp \mu u = x \left( \frac{\zeta_\mu(x^2)}{\zeta_\mu(x^2)} \right)^2 : \quad x = \wp u$$

Hierbei bedeuten  $\zeta_\mu, \zeta_\mu$  die zu einander primen ganzen rationalen Functionen von der Form:

$$\zeta_\mu(y) = y^M + a_1 y^{M-1} + \dots + a_{M-1} y + \mu,$$

$$\zeta_\mu(y) = \mu y^M + a_{M-1} y^{M-1} + \dots + a_1 y + 1,$$

worin  $a_1, a_2, \dots, a_{M-1}$  ganze Zahlen des Körpers  $k(i)$  sind, welche im Falle, wo  $\mu$  eine Primzahl ist, alle durch  $\mu$  teilbar sind, und ferner

$$M = \frac{1}{4}(m-1), \quad m = n(\mu). \quad 1)$$

Ferner sind

$$\frac{cn \mu u}{cn u} \quad \frac{dn \mu u}{dn u}$$

rationale Functionen von  $(sn u)^2$  in  $k(i)$

II.  $\mu$  ist gerade, d.h. teilbar durch  $1+i$ :

$$sn \mu u = sn u, \quad cn u, \quad dn u \quad \frac{f_\mu(x)}{g_\mu(x)} \quad x = sn u$$

worin  $f_\mu(x), g_\mu(x)$  ganze rationale, zu einander prime Functionen in  $k(i)$  sind, und zwar  $g_\mu(x)$  vom Grade  $m$ ,  $f_\mu(x)$  vom Grade  $m-3$

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1) Eisenstein, Beiträge zur Theorie der Elliptischen Functionen, (Mathematische Abh. S. 129.)

oder  $m-4$  jenachdem  $\mu$  durch 2 teilbar ist oder nicht. Eine Ausnahme hievon bildet der Fall, wo

III.  $\mu=1+i$ :

$$\left. \begin{aligned} sn(1+i)u &= \frac{(1+i) sn u}{cn u, dn u} \\ \wp(1+i)u &= \frac{\wp u^2 - 1}{2i \wp u} \end{aligned} \right\} \quad (3)$$

## §. 2.

*Teilung der Periode durch eine ungerade Primzahl in  $k(i)$ .*—Es bedeuete  $\mu$  eine ungerade Primzahl des Körpers  $k(i)$ ,  $m$  die Norm derselben. Die Gleichung  $m-1$ ten Grades in  $x$

$$\zeta_\mu(x^i) = 0 \quad (4)$$

ist nach einem wohlbekannten Satze Eisensteins in  $k(i)$  irreducibel. Die Wurzeln derselben sind die Grössen

$$x_\lambda = sn \gamma^\lambda \frac{\varrho}{\mu} \quad \lambda = 0, 1, \dots, m-2 \quad (5)$$

wenn mit  $\gamma$  eine Primitivzahl nach  $\mu$  bezeichnet wird. Die Gleichung (4) ist cyclisch in dem Rationalitätsbereich  $k(i)$ ; sie definiert einen relativ-cyclischen Körper  $C_\mu$  vom Relativgrade  $m-1$  in Bezug auf  $k(i)$ .

Um die Discriminante  $D$  der Gleichung (4) zu finden, bedienen wir uns der Identität:

$$\begin{aligned} (sn u - sn v)(sn u + sn v) \{sn(u+v) - sn(u-v)\} \\ = 2 sn u, cn u, dn u, sn(u+v) sn(u-v) \end{aligned} \quad (6)$$

worin wir  $sn u, sn v$  der Reihe nach durch alle möglichen Combinationen  $x_\lambda, x_{\lambda'}$  aus den Grössen (5) ersetzen, mit Ausnahme derjenigen für die  $\lambda=\lambda'$  oder  $\lambda \equiv \lambda' \pmod{\frac{m-1}{2}}$  wird; dann nehmen  $sn(u+v)$ ,

$sn(u-r)$  bis auf die Anordnung dieselben Werte. Zusammenmultipliziert und noch vervollständigt mit dem Factor:

$$\left(\prod_{\lambda=0}^{m-2} x_{\lambda}\right)^2 = 2^{3(m-1)} \mu^3 \quad \lambda=0, 1, \dots, m-2$$

ergeben diese Gleichungen:

$$D^2 = 2^{m(m-1)} \mu^{3(m-2)} \left( \prod_{\lambda=0}^{m-2} \cos r^{\lambda} \frac{\partial}{\partial \mu} \right)^{m-2}$$

Lassen wir in der ersten Formel (3)  $u$  die Werte  $r^{\lambda} \frac{\partial}{\partial \mu}$  ( $\lambda=0, 1, \dots, m-2$ ) durchlaufen, so durchläuft  $sn u$  und  $sn(1+i)u$  die Grössenreihe (5), woraus sich ergibt

$$\prod_{\lambda=0}^{m-2} \cos r^{\lambda} \frac{\partial}{\partial \mu} du \cdot r^{\lambda} \frac{\partial}{\partial \mu} = (1+i)^{m-1}$$

sodass endlich

$$D = 2^{\frac{m-1}{2}} \mu^{m-2} \quad (7)$$

### § 3.

*Bestimmung der Discriminante des Körpers  $C_{\mu}$ .*—Es sei nun

$$m-1 = 2^{h_0} p_1^{h_1} p_2^{h_2} \dots$$

die Primzahlzerlegung der rationalen Zahl  $m-1$  im natürlichen Rationalitätsbereich, so besitzt der zu  $k(i)$  relativ-cyclische Körper  $C_{\mu}$  je einen Unterkörper vom Relativgrade  $2^{h_0}, p_1^{h_1}, p_2^{h_2}, \dots$  in Bezug auf  $k(i)$ , welche durch Zusammensetzung den Körper  $C_{\mu}$  erzeugen. Da ein relativcyclischer Körper von einem ungeraden Relativgrade über  $k(i)$  nicht den Factor  $1+i$  in ihrer Relativdiscriminante enthalten kann (§. 11.) so sind nach (7) die Relativdiscriminanten der obenerwähnten Relativkörper vom Relativgrade  $p_1^{h_1}, p_2^{h_2}, \dots$  eine Potenz von  $\mu$ . Weil es aber keinen Relativkörper

über  $k(i)$  gibt, dessen Relativdiscriminante eine Einheit ist, so muss die Zahl  $\mu$  in jedem dieser Unterkörper in so viele identische Primideale zerfallen, wie der Relativgrad des betreffenden Körpers beträgt.

Was den Unterkörper vom Relativgrade  $2^{h_0}$  betrifft, so muss seine Relativdiscriminante gewiss den Factor  $\mu$  enthalten; denn da die Wurzeln der Gleichung (4) aus Paaren entgegengesetzter Zahlen bestehen, und da die Anzahl der Wurzeln  $m-1$  Vielfaches von 4 ist, so sieht man aus

$$x_0 x_1 \dots x_{m-2} = \mu$$

dass die Zahl  $\sqrt{\mu}$  im Körper  $C_\mu$  enthalten sein muss. Diese Zahl  $\sqrt{\mu}$  bestimmt aber einen relativquadratischen Körper über  $k(i)$ , welcher als Teiler in unserem Körper vom Relativgrade  $2^{h_0}$  enthalten ist. Die Relativdiscriminante dieses relativquadratischen Körpers enthält aber gewiss den Factor  $\mu$ , und infolgedessen auch die Relativdiscriminante des Körpers vom Relativgrade  $2^{h_0}$ . Da dieser Körper als ein relativ-cyklischer über  $k(i)$  keinen anderen relativquadratischen Unterkörper ausser  $k(\sqrt{\mu})$  enthalten kann, so folgt aus der Betrachtung des Trägheitskörpers von  $\mu$ , dass  $\mu$  auch in unserem Körper vom Relativgrade  $2^{h_0}$  in  $2^{h_0}$  identischen Primideale zerfallen muss.

Die Zahl  $\mu$  muss hiernach im Körper  $C_\mu$  in  $m-1$  identische Primideale zerfallen; die Relativdiscriminante von  $C_\mu$  enthält  $\mu$  zur  $m-2$ ten Potenz. Dieses Primideal ist ein Hauptideal in  $C_\mu$  und wird durch jede der Wurzeln (5) erzeugt, welche folglich associirte Zahlen sind.

Es handelt sich nun darum, zu entscheiden, ob und inwiefern die Zahl  $1+i$  in der Relativdiscriminante des Körpers  $C_\mu$  enthalten ist.

Ist  $su$  eine beliebige Wurzel der Gleichung (4), so ist  $su(1+i)$  auch Wurzel der Gleichung (4) und als solche associirt mit  $su$ . Es folgt daher aus der Formel (3), dass

$cn\ u, dn\ u$  associirt mit  $1+i$

ist.

Bedeutet nun  $x_1 = sn\ u, x_1' = sn\ v$  zwei beliebige Grösse der Reihe (5), welche jedoch nicht der Gleichung  $x_1 = \pm x_1'$  genügen, so sind  $x_2 = sn(u+v), x_2' = sn(u-v)$  auch Wurzeln der Gleichung (4) und  $x_2 \neq \pm x_2'$ . Es folgt daher aus der Identität (6) dass

$$(x_1 - x_1')(x_1 + x_1')(x_2 - x_2') \text{ associirt mit } (1+i)^3 x_1^3$$

ist; vertauscht man  $v$  mit  $-v$ , was offenbar erlaubt ist, so folgt hieraus dass

$$(x_1 + x_1')(x_1 - x_1')(x_2 + x_2') \text{ associirt mit } (1+i)^3 x_1^3$$

ist, woraus dann folgt:

$$x_2 + x_2' \text{ associirt mit } x_2 - x_2'.$$

Dies gilt aber offenbar für jede zwei Wurzeln  $x, x'$ , die der Gleichung  $x = \pm x'$  nicht genügen.

Es ist daher

$$(x_1 - x_1')^2 (x_2 - x_2') \text{ ass. mit } (1+i)^3 x_1^3;$$

ersetzt man hierin  $u, v$  resp. durch  $u+v, u-v$ , so erhält man

$$(x_2 - x_2')^2 (x_3 - x_3') \text{ ass. mit } (1+i)^3 x_1^3$$

Führt man aber in dieser Weise fort, so gelangt man schliesslich zu:

$$(x_h - x_h')^2 (x_1 - x_1') \text{ ass. mit } (1+i)^3 x_1^3$$

Aus dieser Kette von Beziehungen schliesst man, dass

$$x_1 - x_1' \text{ ass. mit } (1+i) x_1$$

ist.

Mit Hülfe der Gleichungen

$$sn\ 2\ u = \frac{2\ sn\ u, cn\ u, dn\ u}{1 + (sn\ u)^4}$$

$$\operatorname{sn}(-1+2i)u = \operatorname{sn} u \cdot \frac{(\operatorname{sn} u)^4 + (-1+2i)}{(-1+2i)(\operatorname{sn} u)^4 + 1}$$

oder

$$\frac{\operatorname{sn} u - \operatorname{sn}(-1+2i)u}{\operatorname{sn}(-1+2i)u} = \frac{2i(\operatorname{sn} u^4 + 1)}{\operatorname{sn} u^4 + (-1+2i)}$$

schliesst man sodann für  $\mu \neq -1 + 2i$ , d.h.  $m > 5$ , dass

$$\frac{x^4 - 1 + 2i}{4}$$

eine Einheit ist, wenn  $x$  eine beliebige der Wurzeln der Gleichung (4) bedeutet.

Die Discriminante der Gleichung für  $x^4$ ,  $\phi_\mu(x^4) = 0$  ist aber, wie unmittelbar aus (7) folgt,

$$\pm 4^{M(M-1)} \mu^{M-1}, \quad M = \frac{m-1}{4}.$$

Die Discriminante der Zahl  $\frac{x^4 - 1 + 2i}{4}$  in dem durch  $x^4$  definierten Körper ist daher

$$\pm \mu^{M-1}.$$

Hieraus folgt, dass die Relativdiscriminante des Körpers  $k(x^4)$  in Bezug auf  $k(i) = \mu^{M-1}$  also relativ prim zu  $1+i$  ist.

Um die Relativdiscriminante des Körpers  $k(x^2)$  in Bezug auf  $k(x^4)$  zu bestimmen, betrachten wir die Zahl

$$\omega = \frac{i + (\operatorname{sn} u)^2}{\operatorname{cn} u \cdot \operatorname{dn} u}$$

indem wir mit  $\operatorname{sn} u$  eine Wurzel der Teilungsgleichung (4) bezeichnen. Dann ist  $\omega$  eine Zahl des Körpers  $k(x^2)$ , ihre Conjugirte in Bezug auf  $k(x^4)$  ist

$$\omega' = \frac{i - (\operatorname{sn} u)^2}{\operatorname{cn} u \cdot \operatorname{dn} u}$$



Ferner

$$\omega + \omega' = \frac{2i}{cn\,u.\,dn\,u}, \quad \omega\omega' = \frac{1 + (sn\,u)^4}{(cn\,u\,dn\,u)^2}$$

$$\frac{\omega}{\omega'} + \frac{\omega'}{\omega} = \frac{2(1 - sn\,u^4)}{1 + sn\,u^4}$$

woraus unmittelbar folgt, dass diese drei Zahlen mit  $1+i$  associirt sind. Hieraus ergibt sich dass  $\omega$ ,  $\omega'$  ganze und zwar associirte Zahlen sind; da ferner  $\omega\omega'$  mit  $1+i$  associirt ist, so folgt, dass jedes Primideal des Körpers  $k(x^4)$  welches in  $1+i$  aufgeht, in  $k(x^2)$  in zwei identische Primideale zerfällt. Wir setzen demnach

$$(1+i) = \mathfrak{z}\mathfrak{z}'^2 \dots\dots$$

dann wird

$$(\omega) = \mathfrak{z}\mathfrak{z}' \dots\dots$$

Hieraus ergibt sich, dass die Relativedifferente des Körpers  $k(x^2)$  in Bezug auf  $k(x^4)$  dieselbe Potenz der Primideale  $\mathfrak{z}$ ,  $\mathfrak{z}'$ ...enthält, wie die Relativedifferente der Zahl  $\omega$  in Bezug auf  $k(x^4)^{1)}$ . Es ist aber

$$\omega - \omega' = \frac{2\,sn\,u^2}{cn\,u.\,du\,u}$$

Die Relativedifferente des Körpers  $k(x^2)$  in Bezug auf  $k(x^4)$  enthält den Factor  $1+i$  zur ersten Potenz.

Es bleibt nur noch übrig, zu bestimmen, welche Potenzen von  $\mathfrak{z}$ ,  $\mathfrak{z}'$ ...in die Relativediscriminante des Körpers  $C_\mu = k(x)$  in Bezug auf  $k(x^2)$  aufgehen.

Es bedeute wie vorher  $x = sn\,u$  eine beliebige der Wurzeln der Gleichung (4); jede ganze Zahl des Körpers  $C_\mu$  lässt sich dann in der Form darstellen

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1) Vgl. Hilbert, Die Theorie der alg. Zahlkörper, Bericht, erstattet der Deutschen Mathematiker-Vereinigung, S. 392.

$$\gamma = \frac{\alpha + \beta x}{2}$$

wenn  $\alpha, \beta$  ganze Zahlen des Körpers  $k(x^2)$  bedeuten, die der Bedingung

$$\alpha^2 - \beta^2 x^2 \equiv 0 \pmod{4} \quad (8)$$

Genüge leisten. Nun ist die Zahl

$$\xi = 1 + i \operatorname{cn} u$$

gewiss eine ganze Zahl des Körpers  $k(x^2)$  und

$$\xi^2 - x^2 = 2i \operatorname{cn} u \equiv 0 \pmod{\mathfrak{z}^5 \mathfrak{z}^5 \dots}$$

nicht aber für eine höhere Potenz irgend eines  $\mathfrak{z}$  als Modul. Es ist nun zu beweisen, dass eine Congruenz der Form

$$\xi^2 - x^2 \equiv 0 \pmod{\mathfrak{z}^6}$$

überhaupt für eine Zahl  $\xi$  des Körpers  $k(x^2)$  unmöglich ist. In der Tat: wäre  $\xi^2 \equiv x^2 \pmod{\mathfrak{z}^6}$  so müsste erstens  $\xi^2 \equiv \tilde{\xi}^2 \pmod{\mathfrak{z}^5}$ , d.h.  $\xi^2 - \tilde{\xi}^2 = (\xi - \tilde{\xi})(\xi + \tilde{\xi})$  teilbar durch  $\mathfrak{z}^5$ . Dies hätte aber zur Folge, dass  $\xi^2 \equiv \tilde{\xi}^2 \pmod{\mathfrak{z}^6}$  und daher müsste  $\tilde{\xi}^2 - x^2 = (\xi^2 - x^2) - (\xi^2 - \tilde{\xi}^2)$  auch durch  $\mathfrak{z}^6$  teilbar sein, was aber nicht der Fall sein kann.

Wir können nun zeigen, dass die Congruenz (8) dann und nur dann möglich ist, wenn  $\beta$  durch  $1+i$  teilbar ist. Wäre nämlich  $\beta$  nicht durch  $\mathfrak{z}^2$  teilbar, so könnte man, da jedenfalls  $\alpha$  und  $\beta$  durch dieselbe Potenz von  $\mathfrak{z}$  teilbar sein müssen, eine Zahl  $\xi$  aus der Congruenz

$$\alpha \equiv \beta \xi \pmod{\mathfrak{z}^4}$$

bestimmen; es muss dann  $\beta^2 (\xi^2 - x^2)$  durch  $\mathfrak{z}^5$  teilbar sein, und da  $\beta$  nicht durch  $\mathfrak{z}^2$  teilbar sein sollte, so müsste  $\xi^2 - x^2$  wenigstens durch  $\mathfrak{z}^6$  teilbar sein, was aber nicht möglich ist. Es muss daher  $\beta$  durch  $\mathfrak{z}^2$  und ähnlicherweise durch  $\mathfrak{z}^2 \dots$  also durch  $1+i$  teilbar sein.

Ist aber  $\beta$  durch  $1+i$  teilbar, so nehmen wir einfach

$$\alpha = \beta \xi = \beta (1 + i \text{ cn } u)$$

sodass

$$\alpha^2 - \beta^2 x^2 = \beta^2 (\xi^2 - x^2) \equiv 0 \pmod{4}$$

um in

$$\gamma = \frac{\alpha + \beta x}{2}$$

wirklich eine ganze Zahl des Körpers  $C_\mu$  zu erhalten.

Jede ganze Zahl des Körpers  $C_\mu = k(x)$  lässt sich demnach in der Form darstellen

$$\gamma = \frac{\alpha + \beta x}{1+i}$$

worin  $\alpha, \beta$  ganze Zahlen des Körpers  $k(x^2)$  bedeuten, und es existirt wirklich ganze Zahlen in  $k(x)$  bei denen  $\beta$  relativ prim zu  $1+i$  ist.

Wir schliessen daher aus

$$\gamma - \gamma' = (1-i) \beta x$$

dass die Relativedifferenten des Körpers  $C_\mu$  in Bezug auf  $k(x^2)$  den Factor  $1+i$  zur ersten Potenz enthält.

Hiermit haben wir den Satz bewiesen:

*Ist  $\mu$  eine ungerade Primzahl des Körpers  $k(i)$  so ist der Teilungskörper  $C_\mu$  relativ cyclisch vom Relativgrade  $\mu-1$  in Bezug auf  $k(i)$ . Seine Relativediscriminante ist  $2^{m-1} \mu^{m-2}$*

*Ist*

$$m-1 = 2^{h+2} p_1^{h_1} p_2^{h_2} \dots$$

*die Primzahlzerlegung der Zahl  $m-1$ , so ist in  $C_\mu$  als Teiler enthalten je ein relativ cyclischer Körper*

<i>vom Relativgrade</i>	<i>mit der Relativ-</i> <i>discriminante</i>	
$p_1^{\lambda_1}$	$\mu^{p_1^{\lambda_1-1}}$	$(\lambda_1=1, 2, \dots, h_1)$
$p_2^{\lambda_2}$	$\mu^{p_2^{\lambda_2-1}}$	$(\lambda_2=1, 2, \dots, h_2)$
.....	.....	
$2^\lambda$	$\mu^{2^\lambda-1}$	$(\lambda=1, 2, \dots, h)$
$2^{h+1}$	$(1+i)^{2^{h+1}} \mu^{2^{h+1}-1}$	
$2^{h+2}$	$(1+i)^{2^{h+2}} \mu^{2^{h+2}-1}$	

## §. 4.

*Teilung durch eine ungerade Primzahlpotenz.*—Es bedeute wiederum  $\mu$  eine ungerade complexe Primzahl,  $m$  ihre Norm. Die Multiplicationsformel der Function  $sn\ u$  mit dem Factor  $\mu^h$  erhält man durch Iteration aus der Formel

$$sn\ \mu u = x \frac{\phi_1(x^4)}{\chi_1(x^4)} \quad x = sn\ u.$$

Ersetzt man hierin  $x$  durch  $x \frac{\phi_1(x^4)}{\chi_1(x^4)}$ , so kommt nachdem man die Brüche in Nenner und Zähler beseitigt hat

$$sn\ \mu^2 u = x \frac{\eta_2}{\chi_2}$$

$\eta_2$  enthält  $\phi_1$  als Factor; setzt man

$$\eta_2 = \phi_1 \phi_2$$

so ist  $\phi_2$  vom Grade  $\varphi(\mu^2) = m(m-1)$  in  $x$ ; die Coefficient der höchsten Potenz von  $x$  in  $\phi_2$  ist 1, das constante Glied  $\mu$ , die anderen Coefficienten sind alle durch  $\mu$  teilbar.

Durch den Schluss von  $n$  auf  $n+1$  erhält man das allgemeine Resultat:

$$sn \mu^h u = x \cdot \frac{Y_h(x^i)}{X_h(x^i)} \quad x = sn \mu$$

$$Y_h = \zeta_1^{l_1} \zeta_2^{l_2} \dots \zeta_h^{l_h}$$

$\zeta_h$  ist vom Grade  $\varphi(\mu^h) = m^{h-1}(m-1)$  in  $x$ , ihre Coefficienten sind von der oben erwähnten Beschaffenheit. Man erhält daher den Satz:

Die Gleichung  $\varphi(\mu^h) = m^{h-1}(m-1)^{en}$  Grades

$$\zeta_h(x^i) = 0$$

von der die eigentliche  $\mu^h$  Teilung der Periode abhängt ist irreducibel in  $k(i)$ .

Die Discriminante der Gleichung (9) enthält nur die Factoren  $\mu$  und  $1+i$ , wie es sich durch genau dieselbe Betrachtung wie in §. 2. nachweisen lässt.

Um die Gruppe dieser Gleichung zu bestimmen, unterscheiden wir zwei Fälle:

Ist  $\mu = \pi$  nicht reell,  $m = p$  die Noun von  $\pi$ , so gibt es Primitivzahlen nach  $\pi^h$ . Es sei  $g$  eine derselben, dann sind die Wurzeln von (9) die Grösse

$$x_i = sn g^i \cdot \frac{\varrho}{\mu^i} \quad i = 0, 1, \dots, p^{h-1}(p-1)-1.$$

Die Gleichung (9) bestimmt daher einen relativecyclischen Körper vom Relativgrade  $p^{h-1}(p-1)$  in Bezug auf  $k(i)$ . In demselben ist enthalten als Teiler ein relativecyclischer Körper vom Relativgrade  $p^{h-1}$ , dessen Relativediscriminante eine Potenz von  $\pi$  ist, und ein relativecyclischer Körper vom Relativgrade  $p-1$ , welcher nichts anders ist als derjenige, welcher aus der  $\pi$ -Teilung entspringt und welchen wir im vorigen mit  $C_\pi$  bezeichnet haben.

Ist aber  $\mu=q$  reell, also  $m=q^2$ , so lassen sich die  $q^{2(h-1)}(q^2-1)$  incongruenten zu  $q$  relativ primen Zahlclassen des Körpers  $k(i)$  nach dem Modul  $q^h$  ( $h>1$ ) nicht durch die Potenzen einer Zahl repräsentiren. Ist nämlich  $\gamma$  eine Primitivzahl nach  $q$  in  $k(i)$  so ist  $\gamma^{q^2-1} \equiv 1 \pmod{q}$ . Besteht diese Congruenz auch mod.  $q^2$  so nehmen wir statt  $\gamma$ ,  $\gamma + \lambda q$  wo  $\lambda \not\equiv 0 \pmod{q}$  und sind sicher, dass für diese neue Primitivzahl nach  $q$ , die wir einfach mit  $\gamma$  bezeichnen wollen, die obige Congruenz nur für mod.  $q$  besteht; also

$$\gamma^{q^2-1} \equiv 1 + \xi q \quad \xi \not\equiv 0 \pmod{q}$$

Hieraus folgt der Reihe nach

$$\gamma^{q^{(q^2-1)}} \equiv 1 + \xi' q^2 \quad \xi' \not\equiv 0 \pmod{q}$$

.....

$$\gamma^{q^{h-1}(q^2-1)} \equiv 1 + \xi^{(h-1)} q^h \quad \xi^{(h-1)} \not\equiv 0 \pmod{q}$$

Die Zahl  $\gamma$  gehört also mod.  $q^h$  dem Exponenten  $q^{h-1}(q^2-1)$ . Es folgt hieraus, dass für jede ganze Zahl  $\alpha$  des Körpers  $k(i)$  die Congruenz

$$\alpha^{q^{h-1}(q^2-1)} \equiv 1 \pmod{q^h}$$

besteht.

Wenn nun  $\gamma'$  eine Zahl ist, deren Potenz für keinen kleineren Exponenten als  $q^{h-1}$  mod.  $q^h$  congruent mit einer Potenz von  $\gamma$  wird, so werden alle  $q^{2(h-1)}(q^2-1)$  mod.  $q^h$  incongruenten zu  $q$  relativ primen Zahlclassen durch

$$\gamma^\lambda \gamma'^\mu \quad \left( \begin{array}{l} \lambda=0, 1, \dots, q^{h-1}(q^2-1)-1 \\ \mu=0, 1, \dots, q^{h-1}-1 \end{array} \right)$$

repräsentirt.

Um die Existenz einer solchen Zahl  $\gamma'$  nachzuweisen, betrachten wir die Gesamtheit der Zahlen  $\alpha$  die mod.  $q^h$  zum Exponenten  $q^{h-1}$  gehören; für diese Zahlen wird dann  $\alpha \equiv 1 \pmod{q}$  nicht aber

mod.  $q^2$ ; sie sind daher in  $q^2-1$  mod.  $q^2$  incongruenten Zahlclassen von der Form  $a=1+\xi q$  ( $\xi \not\equiv 0$  mod.  $q$ ) enthalten. Von diesen sind nur  $q-1$  verschiedene Classen unter den Potenzen von  $\gamma$  enthalten, nämlich  $\gamma^{\lambda(q^2-1)}$  ( $\lambda=1, 2, \dots, q-1$ .) Wählt man daher  $\gamma'$  beliebig aus den übrigbleibenden Classen, so wird  $\gamma'$  in der That die gesuchte Zahl sein. Denn ist  $a > 0$  der kleinste Exponent, für den  $\gamma'^a \equiv \gamma^a$  (mod.  $q^2$ ) wird, so muss erstens  $a$  in  $q^{h-1}$  aufgehen, sodann muss  $\mu$  teilbar sein durch  $a$  ( $q^2-1$ ) und endlich wenn man  $\mu=ba$  ( $q^2-1$ ) setzt, muss die Zahl  $\gamma' \gamma'^{-b(q^2-1)}$  mod.  $q^h$  zum Exponenten  $a$  gehören. Wäre also  $a < q^{h-1}$  so müsste  $\gamma' \gamma'^{-b(q^2-1)} \equiv 1$  wenigstens mod.  $q^2$ , was aber durch die Wahl von  $\gamma'$  ausgeschlossen ist.

Hiernach lassen sich die Wurzeln der Gleichung (9) für  $\mu=q$  in der Form darstellen

$$x_{\lambda, \mu} = s^{\lambda} \gamma'^{\mu} \frac{\Omega}{q^h} \quad \left( \begin{matrix} \lambda=0, 1, 2, \dots, q^{h-1}(q^2-1)-1 \\ \mu=0, 1, 2, \dots, q^{h-1}-1 \end{matrix} \right)$$

Bezeichnen wir nun die Substitutionen  $(x_{00}, x_{10})$   $(x_{00}, x_{01})$  resp. mit  $s, t$  so ist die Gruppe der Gleichung (9) eine Abel'sche und zwar mit den Elementen

$$s^{\lambda} t^{\mu} \quad \left( \begin{matrix} \lambda=0, 1, 2, \dots, q^{h-1}(q^2-1)-1 \\ \mu=0, 1, 2, \dots, q^{h-1}-1 \end{matrix} \right)$$

Der Teilungskörper ist also in diesem Falle relativ Abel'sch in Bezug auf  $k(i)$ . Dieser enthält als Teiler  $q^{h-1}+1$  von einander verschiedene relativecyclische Körper vom Relativgrade  $q^{h-1}$  in Bezug auf  $k(i)$ . Die Relativediscriminante jedes dieser Körper ist eine Potenz von  $q$ . Der in dem ganzen Teilungskörper enthaltene relativecyclische Unterkörper vom Relativgrade  $q^2-1$  ist nichts anders als derjenige, welcher aus der  $q$ -Teilung entspringt.

## §. 5.

*Teilung durch die Potenz von  $1+i$ .*—Wir bedienen uns in diesem Falle der Function  $\wp u$ : aus der Formel

$$\wp(1+i)u = \frac{\wp u^2 - 1}{2i\wp u}$$

erhält man durch Iteration

$$\wp(1+i)^h u = \frac{f_h(x)}{g_h(x)} \quad x = \wp u$$

worin  $f_h, g_h$  ganze rationale ganzzahlige Functionen in  $k(i)$  sind, welche durch die Recursionsformel

$$\begin{aligned} f_{\lambda+1} &= f_{\lambda}^2 - g_{\lambda}^2 \\ g_{\lambda+1} &= 2i f_{\lambda} g_{\lambda} \end{aligned}$$

in Verbindung mit

$$f_1 = x^2 - 1, \quad g_1 = 2ix$$

vollständig definirt werden.

Die Gleichung  $2^{h-1}$  ten Grades

$$f_h(x) = 0 \tag{10}$$

von welcher die  $(1+i)^h$  Teilung abhängt, lässt sich in  $k(i)$  in vier Gleichungen  $2^{h-2}$  ten Grades zerlegen

$$f_h(x) = (f_{h-2} - i g_{h-2})^2 (f_{h-2} + i g_{h-2})^2 = 0$$

Aus

$$\wp\left(\frac{\varrho}{2}\right) = 1 \quad \wp\left(\frac{\varrho i}{2}\right) = -1$$

folgt durch die Auflösung der Gleichungen

$$\frac{x^2 - 1}{2i x} = \pm 1$$



dass

$$\wp \frac{\varrho}{4} (1+3i) = \wp \frac{\varrho}{4} (3+i) = i$$

$$\wp \frac{\varrho}{4} (1+i) = \wp \frac{\varrho}{4} (3+3i) = -i$$

Die Wurzeln der Gleichung

$$f_{h-2}(x) - i g_{h-2}(x) = 0$$

sind daher die Grössen  $\wp u$  mit

$$u = \frac{\xi + \eta i}{(1+i)^h} \varrho$$

worin

$$(\xi, \eta) \equiv (0, 1), (0, 3), (2, 3), (2, 1), \pmod{4}.$$

Da aber  $\wp(-u) = \wp u$ , so sind diese Grössen enthalten in

$$\wp \frac{\xi + \eta i}{(1+i)^h} \varrho \quad \left( \begin{array}{l} \xi \text{ gerade} \\ \eta \equiv 1 \pmod{4} \end{array} \right)$$

Die Wurzeln der Gleichung

$$f_{h-2}(x) + i g_{h-2}(x) = 0$$

sind die Grössen

$$\wp \frac{\xi + \eta i}{(1+i)^h} \varrho \quad \left( \begin{array}{l} \xi \equiv 1 \pmod{4} \\ \eta \text{ gerade} \end{array} \right)$$

Berücksichtigt man aber dass  $\wp iu = -\wp u$ , so sieht man, dass die beiden Gleichungen denselben Körper definiren.

Da ferner der Körper der  $(1+i)^{\lambda}$ -Teilung in demjenigen der  $(1+i)^{\lambda+1}$ -Teilung als Teiler enthalten ist, wollen wir uns auf die Gleichung der  $(1+i)^{2^m+3}$ -Teilung

$$f_{2^m}(x) + i g_{2^m}(x) = 0 \tag{11}$$

beschränken, deren Wurzeln, die  $2^{2^m}$  Grössen

$$\wp \frac{\xi + \eta i}{(1+i)^{2^{m+3}}} \varrho \quad \left( \begin{array}{l} \xi=1, 5, \dots, 4(2^m-1)+1 \\ \eta=0, 2, \dots, 2(2^m-1) \end{array} \right)$$

sind.

Es sei  $\gamma$  eine ungerade ganze Zahl in  $k(i)$  derart, dass erstens der reelle Teil derselben  $\equiv 1 \pmod{4}$  und zweitens die mit ihr associirte primäre Zahl nicht  $\equiv 1 \pmod{4}$  ist, wie z. B. die Zahl  $1+2i$ . Diese Zahl  $\gamma$  gehört dann  $\pmod{(1+i)^{2^{m+3}}}$  zum Exponenten  $2^m$ ; die  $2^m$  Potenzen von  $\gamma$  mit den Exponenten  $0, 1, 2, \dots, 2^m-1$  sind alle von der Form  $\xi + \eta i$ ,  $\xi \equiv 1 \pmod{4}$ ,  $\eta$ , gerade; und sind mit einander  $\pmod{(1+i)^{2^{m+3}}}$  incongruent. Es existiren nun ebenso wie  $\gamma$  beschaffene Zahlen, unter anderen die zu  $\gamma$  conjugirte Zahl  $\gamma'$ , von welcher keine niedrigere Potenz als die  $2^{m\text{te}}$  mit einer der Potenzen von  $\gamma$   $\pmod{(1+i)^{2^{m+3}}}$  congruent wird. Dann sind die Wurzeln der Gleichung (11) die  $2^{2m}$  Grössen

$$x_{\lambda, \lambda'} = \wp \gamma^{\lambda} \gamma'^{\lambda'} \frac{\varrho}{(1+i)^{2^{m+3}}} \quad (\lambda, \lambda' = 0, 1, 2, \dots, 2^m-1)$$

Die Gleichung (11) reducirt sich nun in eine kette von  $2m$  quadratischen Gleichungen:

$$y_0 = -i = \frac{y_1^2 - 1}{2i y_1}$$

$$y_1 = \frac{y_2^2 - 1}{2i y_2}$$

.....

$$y_{2m-1} = \frac{y_{2m}^2 - 1}{2i y_{2m}}$$

Betrachten wir eine dieser quadratischen Gleichungen

$$y_{n+1}^2 - 2i y_n y_{n+1} - 1 = 0$$

so sehen wir zunächst aus der Discriminante derselben

$$d_{n+1} = -4 (y_n^2 - 1) = -8i y_n y_{n-1}$$

dass, die Discriminante der Gleichung (11) und folglich auch die Relativediscriminante des durch sie definirten Körpers in Bezug auf  $k(i)$  nur den Primfactor  $1+i$  enthalten, da die Zahlen  $y$  sämtlich Einheiten sind.

Ferner leuchtet ein, dass der Körper  $k(y_{n+1})$  durch Adjunction der Zahl  $\sqrt{y_n}$  aus dem Körper  $k(y_n)$  hervorgeht. Um uns zu überzeugen, dass die Gleichung (11) wirklich einen Körper vom Relativgrade  $2^{2^n}$  definirt, genügt es zu zeigen, dass jedesmal der Körper  $k(y_{n+1})$  wirklich von  $k(y_n)$  verschieden ist, oder was dasselbe ist, dass die Zahl  $y_n$  keine Quadratzahl in  $k(y_n)$  ist. Da  $y_1 = 1 \pm \sqrt{2}$ , so ist  $k(y_1)$  wirklich von  $k(i)$  verschieden. Wir nehmen also an, dass  $k(y_n)$  vom Relativgrade  $2^n$  ist, und wollen beweisen, dass dann der Körper  $k(y_{n+1})$  wirklich vom Relativgrade  $2^{n+1}$  sein muss. Wäre nämlich  $y_n = (a + \beta y_{n-1})^2$  worin  $a, \beta$  zwei Zahlen des Körpers  $k(y_{n-1})$  bedeuten, so folgt hieraus, wegen der vorausgesetzten Irreducibilität der Gleichung für  $y_n$  in  $k(y_{n-1})$ , dass

$$\beta^2 = -a^2 = \frac{2 a \beta - 1}{-2i y_{n-1}}$$

d.h.

$$y_{n-1} \pm 1 = \left\{ \frac{1}{(1-i)\beta} \right\}^2$$

Die Norm der Zahl  $y_{n-1} \pm 1$  in Bezug auf  $k(y_{n-2})$  ist aber  $\pm 2i y_{n-2}$ ; es sollte also  $y_{n-2}$  eine Quadratzahl in  $k(y_{n-2})$  sein, was nach der Voraussetzung nicht möglich ist.

Die Gleichung (11) ist daher in  $k(i)$  irreducibel, sie definirt einen relativ Abel'schen Körper vom Relativgrade  $2^{2^n}$  in Bezug auf  $k(i)$ .

Da es keinen Körper über  $k(i)$  mit der Relativediscriminante 1 gibt, und da die Relativediscriminante des Körpers  $k(y_n)$  eine

Potenz von  $1+i$  ist, so folgt dass die Zahl  $1+i$  gleich einer  $2^n$ ten Potenz eines Primideals in  $k(y_n)$  sein muss. Um zu zeigen, dass dieses Primideal ein Hauptideal ist, betrachten wir die Zahl

$$\zeta_n = \frac{2}{y_n - y_{n-1}}$$

des Körpers  $k(y_n)$ . Ihre relative Spur und Norm bez.  $k(y_{n-1})$  sind

$$\zeta_n + \zeta_n' = \frac{2(1+i)}{y_{n-1} - y_{n-2}} \quad \zeta_n \zeta_n' = \frac{i}{y_{n-1}} \cdot \frac{2}{y_{n-1} - y_{n-2}} \quad (12)$$

$\zeta_n$  ist also eine ganze Zahl, wenn  $\zeta_{n-1} = \frac{2}{y^{n-1} - y^{n-2}}$  es ist.  
Die Zahl

$$\zeta_1 = \frac{2}{y_1 - y_0} = \frac{2}{y_1 + i}$$

ist aber eine ganze Zahl, da

$$\zeta_1 + \zeta_1' = -2i \quad \zeta_1 \zeta_1' = -(1+i) \quad (13)$$

Folglich ist  $\zeta_n$  eine ganze Zahl. Die Relativnorm der Zahl  $\zeta_n$  genommen in  $k(y_n)$  und in Bezug auf  $k(i)$  ist nach (12) gleich der Relativnorm von  $\zeta_{n-1}$  genommen in  $k(y_{n-1})$ , bis auf eine Einheit. Es ist also nach (13)

$$N \zeta_n = \varepsilon (1+i)$$

wenn  $\varepsilon$  eine Einheit bedeutet; im Sinne der Idealgleichheit ist demnach

$$(\zeta_n)^{2^n} = (1+i)$$

Hieraus schliesst man ferner dass die Relativedifferente  $\partial_n$  des Körpers  $k(y_n)$  in Bezug auf  $k(y_{n-1})$  der Relativedifferente der Zahl  $\zeta_n$  in Bezug auf  $k(y_{n-1})$  gleich ist; also bis auf eine Einheit

$$\partial_n = (1+i) \zeta_{n-1}$$

Die Relativedifferenten des durch (11) definirten relativ Abel'schen Körpers in Bezug auf  $k(i)$  ist daher

$$\mathfrak{D}_{2^m} = (1+i)^{2^m} \zeta_{2^m-1} \zeta_{2^m-2} \cdots \zeta_3,$$

und endlich die Relativediscriminante

$$D_{2^m} = 2^{(m+1)2^{2^m-1}}$$

Dieser relativ Abel'sche Körper vom Relativgrade  $2^{2^m}$  enthält als Teiler  $2^m+1$  von einander verschiedene relativecyclische Körper vom Relativgrade  $2^m$ , deren Relativediscriminante nur den Primfactor  $1+i$  enthält.

## §. 6.

Durch die bisherigen Auseinandersetzungen wurde die Existenz der folgenden relativ-cyclischen Körper über  $k(i)$  nachgewiesen:

- 1) Eines relativ-cyclischen Körpers vom Relativ-grade  $p^\lambda$  ( $\lambda=1, 2, 3, \dots, h$ ) dessen Relativediscriminante eine Potenz der ungeraden Primzahl  $\mu$  des Körpers  $k(i)$  ist. Hierin bedeutet die Zahl  $h$  den Exponenten der höchsten Potenz von  $p$ , die in  $m-1$  aufgeht, wenn  $m$  die Norm von  $\mu$  in  $k(i)$  ist.
- 2) Eines relativ cyclischen Körpers vom Relativgrad  $p^\lambda$  ( $\lambda$  beliebig) dessen Relativediscriminante eine Potenz von  $\pi$  ist. Hierin bedeutet  $\pi$  eine Primzahl ersten Grades des Körpers  $k(i)$  und  $p$  ihre Norm.
- 3)  $q^\lambda+1$  relativecyclischer Körper vom Relativgrade  $q^\lambda$  ( $\lambda$  beliebig) deren Relativediscriminante eine Potenz von  $q$  ist, wenn  $q$  eine Primzahl zweiten Grades in  $k(i)$  ist.
- 4) Eines relativecyclischen Körpers vom Relativgrade  $2^\lambda$  ( $\lambda=1, 2, \dots, h, h+1, h+2$ ) dessen Relativediscriminante für  $\lambda \leq h$  nur den Factor  $\mu$ , und für  $\lambda=h+1, h+2$  ausserdem nur

noch den Factor  $(1+i)$  enthält. Hierin bedeutet  $\mu$  eine ungerade Primzahl des Körpers  $k(i)$ , und  $2^h$  die höchste Potenz von 2, die in  $\frac{1}{4}(m-1)$  aufgeht, wenn  $m$  die Norm von  $\mu$  ist.

- 5)  $2^\lambda + 1$  relativecyclischer Körper vom Relativgrade  $2^\lambda$  ( $\lambda$  beliebig) deren Relativediscriminante eine Potenz von  $1+i$  ist.

### §. 7.

*Primideale des Teilungskörpers.* Es bedente  $\mu^\lambda$  eine gerade oder ungerade Primzahlpotenz des Körpers  $k(i)$ ,  $K$  den Körper der  $\mu$ -Teilung,  $M$  den Relativgrad desselben in Bezug auf  $k(i)$

Wir haben gezeigt, dass die Primzahl  $\mu$  gleich der  $M^{\text{ten}}$  Potenz eines primen Hauptideals  $\mathfrak{M}$  in  $K$  ist.  $\mathfrak{M}$  ist vom ersten Grade in Bezug auf  $k(i)$

Es sei nun  $\nu$  eine ungerade, primäre, von  $\mu$  verschiedene Primzahl des Körpers  $k(i)$ ,  $n$  deren Norm.

Bedeutet

$$x = sn \ u$$

eine Wurzel der Gleichung der  $\mu^h$  Teilung, so ist jedenfalls

$$x' = sn \ \nu u$$

auch Wurzel derselben Gleichung. Es ist nun

$$x' = x \cdot \frac{x^{n-1} + \nu \gamma}{\nu \gamma' + 1}$$

wenn  $\gamma, \gamma'$  gewisse ganze Zahlen des Körpers  $K$  bedeuten. Es folgt hieraus

$$x' \equiv x^n \pmod{\nu}$$

Eine solche Congruenz besteht aber nicht für eine andere Wurzel  $x''$  der Teilungsgleichung, weil  $x' - x''$  nur durch diejenigen Primideale des Körpers  $K$  teilbar ist, die in  $\mu$  oder in  $1+i$  aufgehen.

Bezeichnen wir nun mit  $s$  die Substitution  $(x, x')$  des Körpers  $K$ , so ist

$$x \mid s^v \equiv x^{n^v}, \quad \dots \quad x \mid s^{\lambda} \equiv x^{n^{\lambda}} \quad (\text{mod. } \nu)$$

Ist daher  $f$  der Grad von  $s$ ,

$$x^{n^f} \equiv x \quad (\text{mod. } \nu)$$

Jede ganze Zahl  $\gamma$  des Körpers  $K$  lässt sich nun in der Form darstellen

$$c. \gamma = a_0 + a_1 x + a_2 x^2 + \dots + a_{M-1} x^{M-1}$$

wenn  $a_0, a_1, \dots, a_{M-1}$  ganze Zahlen des Körpers  $k(i)$  und  $c$  eine gewisse Potenz von  $(1+i)$  bedeuten. Hieraus folgt für jede ganze Zahl des Körpers  $K$

$$\gamma^{n^f} \equiv \gamma \quad (\text{mod. } \nu)$$

Ist daher  $\mathfrak{N}$  ein Primideal des Körpers  $K$ , welches in  $\nu$  aufgeht, und  $n''$  die absolute Norm derselben, so muss  $f' \leq f$ . Da aber

$$x^{n^{f'}} \equiv x \quad (\text{mod. } \mathfrak{N})$$

nicht für  $f' < f$  bestehn kann, so ist  $f' = f$ .

Die Zahl  $f$ , als die Gradzahl der Substitution  $s$ , muss in die Gradzahl  $M$  des Körpers aufgehen; ist  $M = ef$ , so zerfällt die Zahl  $\nu$  in  $e$  von einander verschiedene Primideale in  $K$ . Diese Primideale sind vom  $f^{\text{ten}}$  Grade in Bezug auf  $k(i)$ .

Die Zahl  $f$  ist aber nichts anders als der Exponent, zu welchem die Zahl  $\nu$  gehört mod.  $\mu^h$ .

Es bleibt noch für ungerades  $\mu$  die Zerlegung der Zahl  $1+i$  zu untersuchen. Wir bezeichnen den einzigen Unterkörper von  $K$  vom Index 4 mit  $K'$ , den Relativgrad desselben  $\frac{M}{4}$  mit  $M'$ . Eine Basis von  $K'$  bilden die Potenzen der Zahl  $(\S. 2)$

$$y = \frac{x^4 - a}{4}, \quad a = 1 + 2i$$

sodass jede ganze Zahl  $\gamma$  des Körpers  $K'$  in der Form

$$\gamma = a_0 + a_1 y + a_2 y^2 + \dots + a_{M'-1} y^{M'-1}$$

darstellbar ist, wenn  $a_0, a_1, \dots, a_{M'-1}$  ganze Zahlen des Körpers  $k(i)$  bedeuten.

Nun ist die Zahl

$$x' = sn(1+i)u = \frac{(1+i)sn\ u}{cn\ u\ dn\ u}$$

eine Wurzel der Teilungs-gleichung, und

$$y' = \frac{x'^4 - a}{4}$$

eine zu  $y$  conjugirte Zahl. Es ist aber

$$\begin{aligned} y' &= -\frac{4x^4}{(x^4-1)^2} - \frac{a}{4} = \frac{(4y+a) + a(2y-i)^2}{4(2y-i)^2} \\ &= \frac{-ay^2 + (1-i)a y}{(2y-i)^2} \end{aligned}$$

sodass

$$y' \equiv y^2 \pmod{1+i}$$

Da ferner  $y' - y''$  eine mit  $\mathfrak{M}$  associirte Zahl ist, so besteht eine solche Congruenz nicht für ein anderes  $y''$ .

Hieraus schliesst man genau in derselben Weise wie vorher, dass, wenn  $f$  den kleinsten Exponenten bedeutet, für den

$$(1+i)^f \equiv 1 \pmod{\mu^b}$$

und wenn

$$M' = ef$$

gesetzt wird, die Zahl  $1+i$  in  $e$  von einander verschiedene Primideale in  $K'$  zerfällt.



Wir haben schon bewiesen, dass jedes dieser Primideale in 4 identische Primideale in  $K$  zerfällt; diese Ideale sind daher vom  $f^{\text{ten}}$  Grade in Bezug auf  $k(i)$ .

Die Zerlegung der Primideale des Körpers  $k(i)$  im Körper der  $\mu^h$  Teilung ist daher genau demselben Gesetz unterworfen, wie bei der Kreisteilungstheorie.

Ist  $M = \varphi(\mu^h) = m^{h-1} (m-1)$  so findet in  $K$  die Zerlegung statt:

$$\mu = \mathfrak{M}^w; \quad \mathfrak{M} = \left( sn \frac{\varrho}{\mu^h} \right)$$

$$\nu = \mathfrak{N}_1 \mathfrak{N}_2 \dots \mathfrak{N}_r; \quad ef = M, \quad \nu^f \equiv 1 \pmod{\mu^h}$$

$$1+i = (\mathfrak{Z}_1 \mathfrak{Z}_2 \dots \mathfrak{Z}_s)^t; \quad ef = \frac{M}{4}, \quad (1+i)^f \equiv 1 \pmod{\mu^h}$$

$\mathfrak{M}$  ist vom ersten,  $\mathfrak{N}$ ,  $\mathfrak{Z}$  vom  $f^{\text{ten}}$  Grade in Bezug auf  $k(i)$ .

## §. 8.

*Teilung durch eine Zusammengesetzte Zahl.* Ist  $\lambda$  eine Zusammengesetzte Zahl des Körpers  $k(i)$  und  $\lambda = \mu\nu$  worin  $\mu, \nu$  relativprime Zahlen sind, so durchläuft die Zahl

$$\xi = \eta\mu + \bar{\varepsilon}\nu$$

alle zu  $\lambda$  relativ primen  $\varphi(\lambda)$  incongruenten Zahlclassen mod.  $\lambda$ , wenn man  $\bar{\varepsilon}$  die zu  $\mu$  relativ primen  $\varphi(\mu)$  incongruenten Zahlclassen mod.  $\mu$ , und  $\eta$  die zu  $\nu$  relativ primen  $\varphi(\nu)$  incongruenten Zahlclassen mod.  $\nu$ , durchlaufen lässt.

Setzt man daher

$$w = sn \frac{\bar{\varepsilon}\varrho}{\lambda}, \quad u = sn \frac{\bar{\varepsilon}\varrho}{\mu}, \quad v = sn \frac{\eta\varrho}{\nu}$$

so wird

$$sn w = sn(u+v) = \frac{sn u \, cn v \, dn v + sn v \, cn u \, du u}{1 + sn^2 u \, sn^2 v}$$

und  $sn\ w$  durchläuft alle Wurzeln der Gleichung, von der die eigentliche  $\lambda$ -Teilung abhängt, wenn man in diesem Ausdruck resp.  $sn\ u$ ,  $sn\ v$  alle Wurzeln der Gleichungen der  $\mu$ -,  $\nu$ - Teilung durchlaufen lässt.

Es lassen sich nun jedenfalls  $cn\ u$ ,  $dn\ u$  durch  $sn\ u$ ,  $cn\ v$ ,  $dn\ v$  durch  $sn\ v$  in  $k(i)$  rational ausdrücken, sodass wenn

$$z = sn\ w, \quad x = sn\ u, \quad y = sn\ v$$

gesetzt wird

$$z = f(x, y)$$

und es ist  $f$  eine rationale Function in  $k(i)$ , deren Coefficienten von  $\mu$  und  $\nu$ , nicht aber von der Wahl der Wurzeln  $x$ ,  $y$  abhängen

Der Körper der  $\lambda$ -Teilung ist daher gewiss im demjenigen Körper enthalten, welcher durch die Zusammensetzung der Körper der  $\mu$ - und  $\nu$ - Teilung entsteht.

Jeder Teilungskörper ist daher in einem aus einer Anzahl gewisser elementaren Körper des §. 6. zusammengesetzten Körper enthalten, ist also relativ Abel'sch in Bezug auf  $k(i)$ ; desgleichen auch für jeden Unterkörper eines Teilungskörpers.

Nach Analogie des Hilbert'schen Kreiskörpers nenne ich einen *Lemniscatenkörper* einen jeden Teilungskörper und seinen Unterkörper wie sie im vorigen in Betracht gezogen wurden, sowie einen jeden aus solchen zusammengesetzten Körper.

## §. 9.

Wir kommen nun an den Zielpunkt dieser Abhandlung; es handelt sich darum, nachzuweisen, dass

*jeder im Bereich der rationalen complexen Zahlen Abel'sche Körper ein Lemniscatenkörper ist.*

Da sich jeder Abel'sche Körper aus den cyclischen Körpern, deren Grad eine Primzahlpotenz ist, zusammensetzen lässt, genügt es zu beweisen, dass jeder relativecyclische Körper über  $k(i)$ , dessen Grad eine Primzahlpotenz ist, in einem aus den elementaren Lemniskatenkörpern des §. 6. zusammengesetzten Körper als Teiler enthalten ist.

Wir schicken die folgenden Hilfssätze voran:

- 1) Jeder im natürlichen Rationalitätsbereich Galois'sche Körper, welcher die Zahl  $i$  enthält, und in Bezug auf  $k(i)$  relativ cyclisch ist, ist ein Kreiskörper.

Beweis. Es sei  $K$  ein solcher Körper,  $R$  derjenige Unterkörper von  $K$ , welcher aus allen in  $K$  enthaltenen reellen Zahlen besteht. Da  $K$  als ein im natürlichen Rationalitätsbereich Galois'scher Körper zu jeder seiner Zahlen die conjugirt complexe enthält, und da  $K$  ausserdem die Zahl  $i$  enthält, so muss  $K$  aus  $R$  und  $k(i)$  zusammengesetzt sein.

Der Körper  $K$  kann daher durch eine Zahl  $\theta = \rho + yi$  erzeugt werden, wenn  $\rho$  eine den Körper  $R$  erzeugende Zahl und  $y$  eine passend gewählte rationale Zahl bedeutet. Es sei  $G$  die Gruppe des Körpers  $K$ ; dann hat  $G$  einen Teiler  $C$  vom Index 2, zu welchem die Zahl  $i$  gehört. Diese Untergruppe  $C$  muss aber cyclisch sein, da  $K$  relativcyclisch ist in Bezug auf  $k(i)$ . Durch die Substitutionen dieser Untergruppe gehe  $\theta$  in  $\theta', \theta'', \dots$  und  $\rho$  in  $\rho', \rho'', \dots$  über. Ist sodann  $\theta' = F(\theta)$  worin  $F$  eine rationale Function in  $k(i)$  bedeutet, so ist

$$\rho' + yi = F(\rho + yi)$$

woraus dann folgt

$$\rho' = \Re F(\rho + yi) = \varphi(\rho)$$

worin  $\Re$  für "reeller Teil von" steht. Da  $\theta'' = F(\theta')$  so muss auch

$$\rho'' = \varphi(\rho')$$

sein; also ist  $R$  cyclisch im natürlichen Rationalitätsbereich, und folglich ist  $K$  ein Kreiskörper.

2) Durch Zusammensetzung zweier Abel'scher Körper entsteht wiederum ein Abel'scher Körper. Ist  $A$  ein Abel'scher Körper vom Grade  $m = p^{h_1} p^{h_2} \dots$ , welcher aus den cyclischen Körpern  $C_1, C_2, \dots$  vom Grade  $p^{h_1}, p^{h_2}, \dots$  zusammengesetzt ist,  $B$  ein cyclischer Körper vom Grade  $\kappa = p^k$ , wobei  $k$  keinen der Exponenten  $h_1, h_2, \dots$  übertrifft, habe ferner  $A, B$  einen gemeinsamen Teiler vom Grade  $g$ , so kann der aus  $A$  und  $B$  zusammengesetzte Körper  $K$  auch aus  $A$  und einem zu  $A$  teilerfremden cyclischen Körper vom Grade  $m \cdot g$  zusammengesetzt werden. Als Rationalitätsbereich wird hier jeder beliebige algebraische Körper vorausgesetzt.

Beweis. Es bedeuete  $\alpha, \beta, \kappa = x\alpha + y\beta$  resp. die den Körper  $A, B, K$  erzeugende Zahl. Da sowohl  $\alpha$  als auch  $\beta$  rational durch  $\kappa$ , ausdrückbar sind, so ist, wenn  $\kappa' = x\alpha' + y\beta'$  eine zu  $\kappa$  conjugirte Zahl bedeutet,  $\alpha'$  durch  $\alpha, \beta'$  durch  $\beta$  folglich beide und daher auch  $\kappa'$  rational durch  $\kappa$  ausdrückbar.  $K$  ist daher gewiss ein Galois'scher Körper. Daher gibt es in der Gruppe  $G$  von  $K$  nur eine Substitution, die unter den conjugirten von  $\alpha$ , und unter denjenigen von  $\beta$  eine bestimmte Permutation hervorruft. Die Gesamtheit derjenigen Substitutionen von  $G$ , die die Zahl  $\alpha$  ungeändert lassen, bildet einen Normalteiler  $S$  von  $G$  vom Grade  $n:g$ . Die complementäre Gruppe  $G/S$  ist aber mit der Gruppe des Körpers  $A$  isomorph, also Abel'sch. Dies besagt aber, dass, wenn  $\sigma, \sigma'$  zwei Substitutionen der Gruppe  $G$  sind,  $\sigma\sigma'$  und  $\sigma'\sigma$  dieselbe Permutation unter den conjugirten von  $\alpha$  hervorrufen. Da dasselbe auch in Bezug auf  $\beta$  gelten muss, so rufen  $\sigma\sigma'$  und  $\sigma'\sigma$  dieselbe Permutation unter den conjugirten von  $\beta$  hervor. Es muss daher  $\sigma\sigma' = \sigma'\sigma$ ; der Körper  $K$  ist in der That Abel'sch.

Um den zweiten Teil des Satzes zu beweisen, bemerken wir

zunächst, dass die Gruppe  $S$  cyclisch sein muss, weil der Körper  $B$  nach der Voraussetzung cyclisch ist. Es sei nun  $a_1$  eine den Körper  $C_1$  erzeugende Zahl,  $a_1, a_1', \dots$  ihre conjugirten, ferner seien  $a_2, a_2', \dots; a_3, a_3', \dots; \text{u.s.w.}$  die entsprechenden Zahlen für  $C_2, C_3, \dots$ . Unter den Substitutionen der Gruppe  $G$ , welche nicht in  $S$  enthalten sind, gibt es dann eine, die wir  $s_1$  nennen wollen, welche  $a_1$  zu  $a_1'$  überführt,  $a_2, a_3, \dots$  aber ungeändert lässt; in folge der über den Grad von  $B$  gemachten Annahme ist dann diese Substitution  $s_1$  vom Grade  $p^{h_1}$ . Sind nun  $s_2, s_3, \dots$  ähnliche den Körpern  $C_2, C_3, \dots$  entsprechende Substitutionen, so sind  $s_2, s_3, \dots$  resp. vom Grade  $p^{h_2}, p^{h_3}, \dots$ . Diese Substitutionen  $s_1, s_2, \dots$  erzeugen, eine mit der Gruppe von  $A$  isomorphe Untergruppe  $T$  von  $G$ , vom Grade  $m$ ; und es ist  $G = S.T$ . Zu dieser Untergruppe  $T$  gehört ein Unterkörper  $D$  von  $K$  vom Grade  $n/g$ , und welcher zu  $A$  teilerfremd ist. Es ist daher  $K = A.D$ . Die Gruppe von  $D$  ist aber isomorph mit der complementären Gruppe  $G/T$ , daher auch mit  $S$ , woraus dann folgt, dass  $D$  cyclisch sein muss.

## § 10.

Wir können jetzt den folgenden Satz beweisen:

Es sei  $\mu$  eine Primzahl des Körpers  $k(i)$ ,  $m$  deren Norm,  $p^h$  die höchste Potenz einer natürlichen Primzahl  $p$  die in  $m-1$  aufgeht. Jeder relativecyclische Körper  $F$  vom Relativgrade  $p^{h'}$  ( $h' \leq h$ ) dessen Relativediscriminante keinen Primfactor ausser  $\mu$  enthält, stimmt dann mit dem entsprechenden elementaren Lemniskatenkörper  $C$  überein, deren Existenz in §. 6. nachgewiesen wurde.

Beweis. Wäre  $F$  verschieden von  $C$ , so sei  $K$  der aus  $F$  und  $C$  zusammengesetzte Körper, dessen Relativgrad  $p^n$  gewiss zwischen  $p^{h'}$  und  $p^{2h'}$  liegt;  $K$  enthält keinen relativecyclischen Körper von

höherem als dem  $p^{h'}$ -ten Relativgrad als Teiler. Der Verzweigungskörper von  $\mu$  in  $K$  ist  $K$  selbst, der Trägheitskörper genau vom Grade  $p^{n-h'}$ . Die Annahme  $n > h'$  führt daher zu dem unzulässigen Resultat, dass es einen Relativkörper über  $k(i)$  gibt mit der Relativdiscriminante 1. Es muss daher  $n = h'$ , d.h.  $F = C$ .

Dieser Satz gilt auch für  $p=2$ , wenn  $2^h$  die höchste in  $\frac{1}{4}(m-1)$  aufgehende Potenz von 2 ist.

Wenn die Zahl  $\mu$  in dem obigen Satze reell ist, so ist der entsprechende Körper ein Kreiskörper.

Ist nämlich  $C'$  der in Bezug auf den natürlichen Rationalitätsbereich zu  $C$  conjugirte Körper, so ist  $C'$  auch relativecyclisch über  $k(i)$  und hat dieselbe Relativdiscriminante wie  $C$ . Daher ist  $C = C'$ ; d.h.  $C$  ist ein Galois'scher Körper im natürlichen Rationalitätsbereich, und folglich ein Kreiskörper nach dem Hilfssatz 1. des §. 9.

## §. 11.

Es sei nun  $C_h$  ein relativecyclischer Körper vom Relativgrade  $p^h$ , wo  $p$  eine beliebige natürliche Primzahl bedeutet,  $C_k$  ( $k \leq h$ ) der einzige in  $C_h$  enthaltene relativecyclische Körper vom Relativgrad  $p^k$ . Wir nehmen ferner an, dass die Relativdiscriminante von  $C_h$  eine zu  $p$  relativ prime Primzahl  $\mu$  des Körpers  $k(i)$  sei.

Wäre  $C_{h_0}$  der grösste in  $C_h$  enthaltene Kreiskörper, dessen Relativdiscriminante in Bezug auf  $k(i)$  ausschliesslich den Factor  $p$  enthält, so bezeichnen wir mit  $E_h$  denjenigen Kreiskörper, welcher  $i$  enthält, relativecyclisch vom Relativgrade  $p^h$  in Bezug auf  $k(i)$  ist, und dessen Relativdiscriminante eine Potenz von  $p$  ist. Der grösste gemeinsame Teiler von  $C_h$  und  $E_h$  ist  $C_{h_0}$ . Durch Zusammensetzung der beiden Körper  $C_h$ ,  $E_h$  entsteht dann ein Körper  $K$ ,

welcher auch aus  $E_h$  und einem zu  $E_h$  teilerfremden relativecyclischen Körper  $C^*$  vom Relativgrade  $p^{h-h_0}$  zusammengesetzt wird. Diesen letzten Körper nennen wir dann einfach  $C_h$ , seinen Relativgrad  $p^h$ . Die Relativediscriminante dieses Körpers enthält jedenfalls den Factor  $\mu$ .

Es sei nun  $\zeta$  eine primitive  $p^{hw}$  Einheitswurzel, der durch  $\zeta$  und  $i$  erzeugte Körper  $Z$  ist relativecyclisch in Bezug auf  $k(i)$ . Die Relativgruppe von  $Z$  besteht aus den Potenzen der Substitutionen  $s$ , welche die Zahl  $\zeta$  zu  $\zeta^g$  überführt, wenn  $g$  für ungerades  $p$  eine Primitivzahl nach  $p^h$ , und für  $p=2$ , die Zahl 5 bedeutet.

Die beiden Körper  $C_h$  und  $Z$  haben nach dem obigen keinen gemeinsamen Teiler über  $k(i)$ . Durch ihre Zusammensetzung entsteht ein relativ Abel'scher Körper  $K$ , welcher auch dadurch aus  $Z$  hervorgeht, dass demselben die  $p$ te Wurzel einer gewissen Zahl  $\kappa$  von  $Z$  adjungirt wird, welche der Bedingung genügt, dass

$$\kappa \mid s = \kappa^g \cdot a^{p^h}$$

wenn  $a$  eine Zahl des Körpers  $Z$  bedeutet.

Die Zahl  $\kappa$  kann nicht relativ prim zu  $\mu$  sein; denn wäre  $\kappa$  relativ prim zu  $\mu$ , so müsste die Relativediscriminante von  $K$  in Bezug auf  $Z$ , und folglich auch in Bezug auf  $k(i)$  relativ prim zu  $\mu$  sein, was zur Folge hätte, dass auch die Relativediscriminante von  $C_h$  gegen die Voraussetzung relativ prim zu  $\mu$  ist.

Es sei nun

$$\mu = \mathfrak{M}_1 \cdot \mathfrak{M}_2 \cdot \dots \cdot \mathfrak{M}_r$$

die Zerlegung in die Primideale von  $\mu$  in  $Z$ , und

$$\kappa = \mathfrak{M} \cdot \mathfrak{N}$$

worin  $\mathfrak{M}$  das Product aller in  $\kappa$  aufgehenden Potenzen von  $\mathfrak{M}_1, \mathfrak{M}_2, \dots$  bedeutet, und  $\mathfrak{N}$  infolgedessen prim zu  $\mu$  ist. Es ist dann

$$\zeta = \frac{\kappa | s^e}{\kappa} = \kappa^{e'-1} \zeta^{p^h}$$

eine zu  $\mu$  fremde Zahl. Ist  $p^{h'}$  die höchste Potenz von  $p$ , die in  $g'-1$  aufgeht, so bestimmt die Zahl  $\sqrt[p^{h'}]{\zeta}$  einen Unterkörper von  $K$ , welcher nichts anders ist, als der aus  $C_{h-h'}$  und  $Z$  zusammengesetzte Körper. Es folgt dann, dass die Relativdiscriminante von  $C_{h-h'}$  prim zu  $\mu$  ist.

Ist anderseits  $m$  die Norm von  $\mu$  und  $p^a$  die höchste Potenz von  $p$ , die in  $m-1$  aufgeht, so wird

$$m^{p^{h-a}} \equiv 1 \pmod{p^h}$$

und  $p^{h-a}$  ist zugleich der kleinste Exponent, für den diese Congruenz bestehen kann. Dann zerfällt die Zahl  $\mu$  in  $e=p^{a-1}(p-1)$  von einander verschiedene Primideale in  $Z$ ; und zugleich ist  $p^a$  die höchste Potenz von  $p$ , die in  $g'-1$  aufgeht. Es ist also  $a=h'$ , und wir schliessen:<sup>1)</sup>

*Damit  $\mu$  in der Relativdiscriminante von  $C_k$  als Factor auftreten kann, ist es notwendig, dass*

$$m \equiv 1 \pmod{p^{h-k+1}}$$

Sollte daher die Zahl  $\mu$  überhaupt in der Relativdiscriminante von  $C_h$  auftreten können, so muss  $m-1$  durch  $p$  teilbar sein; sollte  $\mu$  schon in der Relativdiscriminante von  $C_1$  auftreten, so muss  $m \equiv 1 \pmod{p^h}$ .

## §. 12.

Trete die Zahl  $\mu$  in der Relativdiscriminante von  $C_1$  auf, sodass

1) Dies ist die Verallgemeinerung des Hilbert'schen Satzes (l.c. S. 342.) in etwas schärferer Fassung. Hierzu ist zu vgl.: A. Wiman, zur Theorie der relativabelschen Zahlkörper, Acta Univ. Lundensis 36, welche Abhandlung mir nur dem Berichte in den "Fortschritte der Mathematik (Jahrgang 1900) nach bekannt ist.



$m \equiv 1 \pmod{p^h}$ , so sei  $M$  derjenige relativecyclische Körper vom Relativgrade  $p^h$ , dessen Relativediscriminante ausschliesslich den Primfactor  $\mu$  enthält. Möglicherweise haben dann  $C_h$  und  $M$  einen gemeinsamen Teiler ausser  $k(i)$ . Der zusammengesetzte Körper  $C_h M$  ist dann relativ Abelsch vom Relativgrade  $p^{h+h'}$  ( $h' \leq h$ ) in Bezug auf  $k(i)$ . Seine Relativgruppe  $G$  ist von der Form

$$s^{\lambda} t^{\mu}, \quad \left( \begin{array}{l} \lambda=0, 1, \dots, p^h-1; \quad s^{p^h}=1 \\ \mu=0, 1, \dots, p^{h'}-1; \quad t^{p^{h'}}=1 \end{array} \right)$$

Die Trägheitsgruppe  $T$  der Zahl  $\mu$  in  $C_h M$  ist cyclisch und vom Grade  $p^h$ ;  $T$  besteht daher aus den Potenzen einer Substitution  $s^{\lambda}$ . Der Trägheitskörper ist vom Relativgrade  $p^{h'}$ ; die Gruppe desselben ist isomorph mit der complementären Gruppe  $G/T$ , und daher cyclisch. Der Trägheitskörper ist demnach relativecyclisch in Bezug auf  $k(i)$ , wir nennen ihn  $C'_{h'}$ . Dieser hat keinen Teiler ausser  $k(i)$  mit  $M$  gemein. Daher ist

$$C_h M = C'_{h'} M;$$

die Relativediscriminante von  $C'_{h'}$  enthält alle in der Relativediscriminante von  $C_h$  auftretenden Primfactoren mit Ausnahme der Zahl  $\mu$ .

Wir nehmen jetzt allgemein an, die Zahl  $\mu$  trete erst in der Relativediscriminante von  $C_{k+1}$  auf, sodass  $m \equiv 1 \pmod{p^{h-k}}$ . Es existirt daher ein relativecyclischer Körper  $M$  vom Relativgrade  $p^{h-k}$ , dessen Relativediscriminante eine Potenz von  $\mu$  ist. Nach dem vorhin gesagten, können wir nun annehmen, dass  $C_h$  und  $M$  keinen gemeinsamen Teiler ausser  $k(i)$  besitzen. Der zusammengesetzte Körper  $MC_h$  ist dann relativ Abelsch vom Relativgrade  $p^{2h-k}$ , die Relativgruppe  $G$  desselben von der Form

$$s^\lambda t^\mu, \quad \left( \begin{array}{l} \lambda=0, 1, 2, \dots, p^h-1; \quad s^{2^{2^h}}=1. \\ \mu=0, 1, 2, \dots, p^{h-k}-1; \quad t^{p^{h-k}}=1. \end{array} \right)$$

worin  $s, t$  resp. die Substitutionen bedenten, welche den Körper  $M, C_h$  ungeändert lassen. Dann gehört der Unterkörper  $C_k$  zu der Untergruppe  $G'$  von der Form

$$s^{*\lambda} t^\mu, \quad \left( \begin{array}{l} \lambda, \mu=0, 1, \dots, p^{h-k}-1. \\ s^*=s^{p^k} \end{array} \right)$$

Nimmt man daher  $C_k$  zum Rationalitätsbereich, so wird  $G'$  die Relativgruppe von  $MC_h$  in diesem Rationalitätsbereich.

In  $C_k$  zerfalle  $\mu$  in eine Anzahl von einander verschiedener Primideale, etwa  $\mu=\mathfrak{M}\mathfrak{M}'\dots$ . Ist nun  $\mathfrak{M}^*$  das Primideal des Körpers  $MC_h$ , welches in  $\mathfrak{M}$  aufgeht, so muss  $\mathfrak{M}^*$  wenigstens zur  $p^{h-k}$ -ten Potenz in  $\mathfrak{M}$  enthalten sein; die Trägheitsgruppe von  $\mathfrak{M}$  in dem Relativkörper  $MC_h$  muss daher wenigstens vom Grade  $p^{h-k}$  sein. Die Verzweigungsgruppe von  $\mathfrak{M}$  ist aber eine Einheitsgruppe. Daher muss die Trägheitsgruppe von  $\mathfrak{M}$  cyclisch sein, und da es in  $G'$  keinen cyclischen Teiler von einem höheren als  $p^{h-k}$ -ten Grade gibt, so muss die Trägheitsgruppe von  $\mathfrak{M}$  genau vom Grade  $p^{h-k}$  sein. Daraus folgt, dass  $\mathfrak{M}^*$  genau zu der  $p^{h-k}$ -ten Potenz in  $\mathfrak{M}$  und folglich in  $\mu$  enthalten sein muss.

Wir kehren nun zu dem ursprünglichen Rationalitätsbereich  $k(i)$  zurück. Die Trägheitsgruppe  $T$  von  $\mathfrak{M}^*$  ist cyclisch und vom Grade  $p^{h-k}$ , der Trägheitskörper  $C'_h$  von  $\mathfrak{M}^*$  ist vom Relativgrade  $p^h$ , und es ist  $MC_h=MC'_h$ . Die Gruppe  $T$  besteht daher aus den Potenzen einer Substitution von der Form  $s^t$ . Die Gruppe des Körpers  $C'_h$ , isomorph mit  $G/T$ , ist also cyclisch, sodass  $C'_h$  relativecyclisch in Bezug auf  $k(i)$  ist. Die Relativediscriminante von  $C'_h$  enthält alle in derjenigen von  $C_h$  auftretenden Primfactoren mit Ausnahme der Zahl  $\mu$ .

Wir operiren sodann in ähnlicher Weise mit dem Körper  $C'$ , falls die Relativediscriminante desselben noch eine zu  $p$  prime Primzahl  $\mu'$  enthält, und erhalten dann einen Körper  $C''$ , dessen Relativediscriminante alle in derjenigen von  $C$  vorkommenden Primfactoren enthält mit Ausnahme der Zahlen  $\mu, \mu'$ .

Fahren wir aber in dieser Weise fort, so gelangen wir schliesslich zu einem relativecyclischen Körper  $C''$  vom Relativgrade  $p^{h^*}$  ( $h^* \leq h$ ) dessen Relativediscriminante nur noch die in  $p$  aufgehenden Primzahlen des Körpers  $k(i)$  enthält.

Es handelt sich hiernach nur noch darum, unseren Hauptsatz für einen solchen Körper zu beweisen.

### §. 13.

*Jeder relativ cyclische Körper von Relativgrade  $p$ , dessen Relativediscriminante eine Potenz von  $\pi$  ist, stimmt mit dem entsprechenden elementaren Lemniskatenkörper überein, deren Existenz in §. 6. nachgewiesen wurde ;* hierin bedeutet  $p$  eine natürliche Primzahl von der Form  $4h+1$ , und  $\pi$  einen Primfactor von  $p$  in  $k(i)$

Beweis. Gebe es zwei verschiedene Körper  $C, C'$  von der angegebenen Beschaffenheit, so entsteht durch ihre Zusammensetzung und die Adjunction einer primitiven  $p^{\text{ten}}$  Einheitswurzel  $\zeta$  ein Körper  $K$  vom Relativgrad  $p^2(p-1)$ .

In dem durch  $\zeta$  und  $i$  erzeugten Körper  $Z$  zerfällt  $p$  in  $2(p-1)$  Primideale ersten Grades

$$(\rho) = (\mathfrak{p}\mathfrak{p}')^{p-1}$$

und es ist

$$p = \pi\pi' ; \quad \pi = \mathfrak{p}^{p-1}, \quad \pi' = \mathfrak{p}'^{p-1} \quad (\zeta) = (1 - \zeta) = \mathfrak{p}\mathfrak{p}'$$

Der Körper  $k(C, \zeta)$  geht dadurch aus  $Z$  hervor, dass man diesem

letzteren die  $p$ te Wurzel einer Zahl  $\kappa$  von  $Z$  adjungiert. Diese Zahl  $\kappa$  genügt der bekannten Bedingung<sup>1)</sup>

$$\kappa \mid s = \kappa^q. a^p$$

Wir können aber  $\kappa$  so wählen, dass  $\kappa \equiv 1 \pmod{\mathfrak{p}}$  wird; denn leistet  $\kappa$  dieser Bedingung nicht Genüge, so können wir statt  $\kappa$  eine Zahl  $\kappa^*$  von der Form

$$\kappa^* = a^{p(p-1)} \left( \frac{\kappa \mid s}{\kappa} \right)^{p-1}$$

nehmen, wobei wir die natürliche ganze Zahl  $a$  passend wählen, und erhalten in  $\kappa^*$  eine ganze Zahl, der die Eigenschaft zukommt, dass

$$(c) \quad \kappa^* \mid s = \kappa^{*q-1} a^{*p},$$

$$k(C, \zeta) = k(\zeta, \sqrt[p]{\kappa^*}) \quad \kappa^* \equiv 1 \pmod{\mathfrak{p}}$$

Da nun  $\mathfrak{p}$  ein Primideal ersten Grades ist, auch in Bezug auf den natürlichen Rationalitätsbereich, so wird die Congruenz

$$\kappa^* \equiv 1 + a\eta \pmod{\mathfrak{p}^2}$$

$$(\eta = 1 - \zeta)$$

durch eine natürliche ganze Zahl  $a$  befriedigt. Hierbei kann aber nicht  $a \equiv 0 \pmod{p}$  sein. Wäre nämlich  $a$  durch  $p$  teilbar, so wird  $\kappa^* \equiv 1 \pmod{\mathfrak{p}^2}$ , woraus mit Hülfe von (c) folgt

$$\kappa^* \equiv 1 \pmod{\mathfrak{p}^n}$$

Ist nun  $\nu$  eine durch  $\mathfrak{p}'$  aber nicht durch  $\mathfrak{p}$  teilbare ganze Zahl des Körpers  $Z$ , so ist die Zahl

$$\omega = \frac{\nu}{\eta} (1 - \sqrt[p]{\kappa^*})$$

welche der Gleichung  $(\lambda\omega - \nu)^p + \nu^p \kappa^* = 0$  genügt, eine ganze Zahl.

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1) Vgl. z. B. Hilbert, l.c.

Die Zahl  $\omega$  erzeugt aber offenbar den Körper  $k(C', \xi)$ . Die Relativediscriminante dieser Zahl in Bezug auf  $Z$  ist  $2^{p(p-1)} \kappa'^{p-1}$ , also prim zu  $p$ . Daher muss die Relativediscriminante von  $k(C', \xi)$  in Bezug auf  $Z$  auch prim zu  $p$  sein. Bedeutet nun  $\mathfrak{p}$  ein Primideal des Körpers  $k(C', \xi)$ , welches in  $p$  aufgeht, so geht  $\mathfrak{p}$  nur zu der  $p$ -ten Potenz in  $\pi$  auf. Der Trägheitskörper von  $\pi$  ist dann vom Relativgrade  $p$  in Bezug auf  $k(i)$ , und seine Relativediscriminante muss 1 sein, was aber unmöglich ist. Es ist daher

$$\kappa^* \equiv 1 + a\eta \pmod{\mathfrak{p}^2}, \quad a \not\equiv 0 \pmod{p}$$

Genau dieselbe Erwägungen führen uns zu dem Resultat:

$$k(C', \xi) = k(\xi, \sqrt[p]{\rho})$$

mit 
$$\rho \equiv 1 + b\eta \pmod{\mathfrak{p}^2}$$

wo 
$$b \not\equiv 0 \pmod{p}$$

Bestimmt man nun die natürliche ganze Zahl  $c$  aus der Congruenz

$$a + bc \equiv 0 \pmod{p}$$

so folgt

$$\theta \equiv \kappa^*, \quad \rho^c \equiv 1 \pmod{\mathfrak{p}^2}$$

und es ist

$$\theta^{-s} \equiv \theta^{r-1}, \quad \gamma^p$$

Wäre also  $C \neq C'$  so würde  $\theta$  gewiss nicht eine  $p$ -te Potenz in  $Z$  sein. Da aber  $k(\xi, \sqrt[p]{\theta})$  gewiss in  $K = k(C', C', \xi)$  enthalten ist, würde die Congruenz  $\theta \equiv 1 \pmod{\mathfrak{p}^2}$  genau wie vorher zu einem unzulässigen Resultat führen. Demnach muss, wie bewiesen werden sollte,

$$C = C'.$$

---

*Jeder relativcyclische Körper vom Relativgrade  $p^h$ , dessen Relativ-*

*discriminante eine Potenz von  $\pi$  ist, stimmt mit dem entsprechenden elementaren Körper des §. 6. überein.*

Um den Satz durch vollständige Induction zu beweisen, nehmen wir ihn als bewiesen an, für alle kleinere Werte von  $h$ . Sind sodann  $C, C'$  zwei verschiedene Körper von der angegebenen Beschaffenheit, so müssen die in ihnen enthaltenen relativecyclischen Körper vom Relativgrad  $p^{h-1}$  auf Grund der Voraussetzung mit einander übereinstimmen. Durch Zusammensetzung entsteht daher aus  $C, C'$  ein Körper  $K$  vom Relativgrad  $p^{h+1}$ , welcher auch aus  $C$  und einem zu  $C$  teilerfremden relativecyclischen Körper  $C_1$  vom Relativgrad  $p$  zusammengesetzt werden kann. Da aber die Relativediscriminante von  $C_1$  nur den Primfactor  $\pi$  enthalten kann, und da  $C_1$  nicht in  $C$  enthalten sein soll, so musste die Relativediscriminante von  $C_1$  gleich 1 sein, was unmöglich ist.

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Die beiden elementaren Körper vom Relativgrade  $p^h$ , deren Relativediscriminante resp. eine Potenz von  $\pi$  und  $\pi'$  sind bezeichnen wir bez. mit  $H_p$  und  $H'_p$ . Durch die Zusammensetzung der beiden entsteht ein relativ Abel'scher Körper  $P_p$  vom Relativgrade  $p^{2h}$ ; in demselben sind enthalten als Teiler die  $p^h+1$  von einander verschiedenen relativecyclischen Körper vom Relativgrad  $p^h$ , deren Relativediscriminante ausschliesslich die Primzahlen  $\pi, \pi'$  enthalten. Es ist jetzt zu beweisen, dass es ausser diesen keinen Körper von dieser Beschaffenheit gibt.

Es wird genügen, den Satz nur für den Fall, wo  $h=1$ , zu beweisen; das übrige folgt unmittelbar durch die vollständige Induction.

Es sei also  $C$  ein relativecyclischer Körper vom Relativgrad  $p$ , dessen Relativediscriminante ausschliesslich die Primzahlen  $\pi, \pi'$  enthält,

$\zeta$  wie vorher eine primitive  $p^h$  Einheitswurzel,  $\mathfrak{p}, \mathfrak{p}'$  die beiden von einander verschiedenen Primideale des Körpers  $Z=k(\zeta, i)$ , die in  $p$  aufgehen.

Wir betrachten nun die Zahl  $\kappa$ , welche in der bekannten Weise den Körper  $C/Z$  erzeugt. Wir nehmen wie vorher an, es sei

$$\kappa \equiv 1 + a\zeta \pmod{\mathfrak{p}^2}$$

$$a \not\equiv 0 \pmod{p}$$

sodass

$$\rho = \zeta^{-a} \kappa \equiv 1 \pmod{\mathfrak{p}^2}$$

Bezeichnen wir nun die Körper  $k(C, \sqrt[p]{\zeta})$ ,  $k(\zeta, \sqrt[p]{\rho})$  bez. mit  $K$ ,  $K'$ , so ist  $K'$  gewiss in  $K$  enthalten. Die Relativediscriminante von  $K'$  in Bezug auf  $Z$  ist aber prim zu  $\mathfrak{p}$ , sie muss daher ausschliesslich den Primteiler  $\mathfrak{p}'$  enthalten, sodass  $K=k(Z, H_1')$  sein muss. Ähnlicherweise enthält  $K$  auch den Körper  $ZH_1$  als Teiler. Daher ist

$$K=Z, P_1$$

woraus dann folgt, dass in der That  $C$  in  $P_1$  enthalten sein muss, q. e. d.

#### §. 14.

Wir haben gesehen, dass es  $q^h+1$  von einander verschiedene relativecyclische Körper vom Relativgrade  $q^h$  gibt, deren Relativediscriminanten ausschliesslich den Primfactor  $q$  enthalten, dass diese  $q^h+1$  Körper Teiler eines relativ Abelschen Körpers  $Q_h$  vom Relativgrad  $q^{2h}$  sind; hierbei bedendet  $q$  eine natürliche Primzahl von der Form  $4h+3$ , sodass  $q$  eine Primzahl zweiten Grades in  $k(i)$  ist.

Wir wollen jetzt zeigen, dass es ausser diesen keinen anderen Körper von der angegebenen Beschaffenheit gibt; begnügen uns aber auch hier den Satz nur für den Fall, wo  $h=1$  ist, zu beweisen.

Da es nur einen Kreiskörper gibt, welcher relativcyclisch über  $k(i)$  vom Relativgrade  $q$  ist, und dessen Relativediscriminante nur den Primfactor  $q$  enthält, nämlich denjenigen, welcher in dem durch  $i$  und eine primitive  $q^2$ te Einheitswurzel erzeugten Körper enthalten ist, so sind wir sicher, dass es einen Körper  $C$  von der angegebenen Beschaffenheit gibt, der kein Kreiskörper ist, und infolgedessen von dem in Bezug auf den natürlichen Rationalitätsbereich zu  $C$  conjugirten Körper  $C'$  verschieden ist (§. 8), so-dass  $CC' = Q_1$ . Der Körper  $Q_1$  enthält aber den oben erwähnten Kreiskörper als Teiler; bedeutet daher  $\zeta$  eine primitive  $q^2$ te Einheitswurzel, so wird  $k(Q_1, \zeta) = k(C, \sqrt[q]{\zeta})$  sein. Gebe es nun einen Körper  $\bar{C}$  von der angegebenen Beschaffenheit, der jedoch nicht in  $Q_1$  enthalten ist, so entsteht durch Composition ein relativ Abel'scher Körper  $k(Q_1, \bar{C}, \zeta) = k(C', C, \sqrt[q]{\zeta})$  vom Relativgrad  $q^3(q-1)$ .

Bezeichnen wir nun mit  $Z$  den durch  $i$  und  $\zeta$  erzeugten Körper, so ist die Zahl  $q$  die  $(q-1)^{te}$  Potenz eines Primideals  $\mathfrak{q}$  in  $Z$ , welches vom zweiten Grade in Bezug auf den natürlichen Rationalitätsbereich, aber vom ersten in Bezug auf  $k(i)$  ist; es ist ferner  $\mathfrak{q}$  das durch die Zahl  $\eta = 1 - \zeta$  erzeugte Hauptideal.

Wir denken uns nun die Zahlen  $\kappa, \theta$  wie im vorigen Paragraphen aufgestellt, sodass

$$k(\zeta, C) = k(\zeta, \sqrt[q]{\kappa}); \quad \kappa \mid s = \kappa^{q-1} \alpha^q; \quad \kappa \equiv 1 \pmod{\mathfrak{q}} \not\equiv 1 \pmod{\mathfrak{q}^2}$$

$$k(\zeta, \bar{C}) = k(\zeta, \sqrt[q]{\theta}); \quad \theta \mid s = \theta^{q-1} \beta^q; \quad \theta \equiv 1 \pmod{\mathfrak{q}} \not\equiv 1 \pmod{\mathfrak{q}^2}$$

Da  $\mathfrak{q}$  ein Primideal ersten Grades in Bezug auf  $k(i)$  ist, so können wir zwei nicht durch  $q$  teilbare ganze Zahlen des Körpers  $k(i)$  finden, sodass

$$\kappa \equiv 1 + (a + bi)\eta \pmod{\mathfrak{q}^2}$$

$$\theta \equiv 1 + (a' + b'i)\eta \pmod{\mathfrak{q}^2}$$



Nehmen wir noch die Congruenz zu Hilfe

$$\zeta^r \equiv 1 - rz \pmod{q^2}$$

und setzen

$$\rho = \zeta^r u, \quad \theta^r \equiv 1 + (u + iv)z \pmod{q^2}$$

so ist

$$u = a + ca' - r, \quad r = b + cb'.$$

Man kann nun die natürlichen ganzen Zahlen  $c, r$  so bestimmen, dass

$$u \equiv 0, \quad r \equiv 0 \pmod{q}$$

wird. Dann ist

$$\rho \equiv 1 \pmod{q^2}$$

wir können nun genau in derselben Weise fortfahren wie im vorigen Paragraphen, um nuns zu überzeugen, dass der Körper  $\bar{C}$  in der Tat in  $Q_1$  enthalten ist.

## §. 15.

Um endlich den entsprechenden Satz für den Fall zu beweisen, wo der Relativgrad eine Potenz von 2, und die Relativediscriminante eine Potenz von  $1+i$  ist, betrachten wir den relativ Abelschen Körper  $D_1$  vom Relativgrad 4, welcher aus der Teilung der Periode von  $\wp(u)$  durch  $(1+i)^7$  entspringt. Dieser Körper ist durch die Zahl  $y$  erzeugt, welche der Gleichung genügt:

$$y^2 - 2ixy - 1 = 0$$

$$(x^2 - 2x - 1 = 0)$$

Es ist aber

$$D_1 = k(y) = k(\sqrt{x}, i) \quad x = 1 \pm \sqrt{2}$$

Setzt man nun

$$\alpha = \sqrt{2} + 1 \quad \beta = \sqrt{2} - 1$$

so wird

$$2(1 \pm i) = (\sqrt{\alpha} \pm i\sqrt{\beta})^2$$

$D_1$  enthält daher  $\sqrt{1+i}$ ,  $\sqrt{1-i}$ , und demnach auch  $\sqrt{i}$ . Die drei in  $D_1$  enthaltenen relativ quadratischen Körper, sind  $k(\sqrt{1+i})$ ,  $k(\sqrt{1-i})$  und  $k(\sqrt{i})$ .

Anderseits leuchtet ein, dass es ausser diesen, keinen relativ quadratischen Körper gibt dessen Relativdiscriminante eine Potenz von  $1+i$  ist.

Hieraus schliesst man durch vollständige Induction, dass es ausser den in §. 6. (5) angegebenen, keinen anderen Körper ihrer Art gibt.

Göttingen, im Frühjahr, 1901.



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# Modulus of Rigidity of Rocks \*

AND

## Hysteresis Function.

BY

S. KUSAKABE, *Rigakushi.*

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With Plates I—XXII, containing 53 Figures.

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### INTRODUCTION.

Since Galileo Galilei<sup>(1)</sup> published his inquiries concerning the rupture and strength of beams in 1638, the elastic nature of substances

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\* Detailed descriptions of the experiments are to be found in "The Publications of the Earthquake Investigation Committee in Foreign Languages," No. 14, Tokyo, 1903.

(1) Galileo Galilei. Thomas Salisbury's Mathematical Collections and Transactions; London, 1655. Vol. II.

has from time to time been investigated by many scores of distinguished physicists and engineers. Indeed, the questions of elasticity, having close relation, on one hand, to the strength of materials, and, on the other to almost every branch of physics constitute a problem whose solution has long been hoped for, but not yet solved, either from its theoretical or its practical side.

A law expressed by Hooke<sup>(1)</sup> with Latin terseness in the words "*Ut tensio, sic vis*" is the foundation of the mathematical theory of elasticity taken in the wide sense. The result of experimental researches is that Hooke's law is nearly fulfilled, for all hard solids, each through the whole range within its limits of elasticity.

Coulomb first gave his theory of torsion for hairs and silk threads<sup>(2)</sup> and then extended it to metal threads.<sup>(3)</sup> He brings out clearly that the set-slide,—i.e. non-elastic permanent strain—produced by torsion is at first proportional to the total slide and then to the elastic slide, and that the slide-modulus (*réaction de torsion*) remains almost the same after any slide-set, that the elastic limit (at least in the case of torsion) can be extended by giving the material a set. Savart<sup>(4)</sup> endeavoured to extend experimentally the result which Coulomb had obtained for the torsion of a wire, and concluded thus :—" Quelque soit le contour de la section transversale der verges, les arcs de torsion sont directement proportionnels au moment de la force et à la longueur."

The first formula for the torsion of square and rectangular prisms, which was given by Eaton Hodgkinson,<sup>(5)</sup> has been proved to

(1) Hooke. *De potentiâ restitutiva*; London, 1678.

(2) Coulomb. *Mémoires des savants étrangers*. Tom. IX. 1777.

(3) Coulomb. *Histoire de l'Académie des Sciences*, année 1784. Paris, 1787.

(4) Savart. *Annales de chimie et de physique*. Tom. 41, 1829.

(5) E. Hodgkinson. *Experimental researches on the strength and other properties of cast iron*, 1846.

be inexact by the later researches of Saint-Venant.<sup>(1)</sup> Vicat<sup>(2)</sup> probably was the first elastician who published a well-considered experiment on yielding. In a paper "De fili Bombycini vi elastica," Göttingen 1841, Weber<sup>(3)</sup> wrote ".....deuplex tensionis effectus..... alter primarius seu momentaneus ac subitus, alter secundarius seu subsequens et continuatus....." It is then noted that this "prolongatio continuata" is not permanent. An experimental discussion of set and yielding is found in a memoir entitled "Sur la torsion des fils métalliques et....." written by Ignace Giulio.<sup>(4)</sup> His conclusion is instructive: "L'altération de forme produite par l'action d'une force extérieure sur un corps elastique se compose de deux parties: l'une indépendante de la durée de cette action et sensiblement proportionnelle à son intensité; l'autre, croissant plus rapidement que la force qui la produit, et suivant une fonction de la durée de son action." Then he says that when the external force ceases to act, the first part of the deformation disappears instantaneously, but the second part persists, diminishing, however, continuously with the lapse of time.

G. Wiedemann,<sup>(5)</sup> in his paper "Ueber die Torsion," concludes that the temporary torsions of a wire twisted for the first time by increasing loads increase more rapidly than these loads, and that the torsional sets or torts of the wire increase still more rapidly. In a paper entitled "Memoire sur la torsion," G. Wertheim<sup>(6)</sup> also divides

(1) Saint-Venant. Memoire sur la torsion des prismes; Comptes Rendus, Tom. XXXVI. 1853.

(2) Vicat. Annales des ponts et chaussés, 1<sup>er</sup> semestre, 1834.

(3) W. Weber. W. Weber's Werke, herausgegeben v. d. Königl. Gesel. d. Wiss. zu Göttingen. Bd. I. pp. 447-474.

(4) Ignace Giulio. Memorie della reale Accademie delle Scienze di Torino. Serie II. Tomo. IV. 1842.

(5) G. Wiedemann. Pogg. Annalen. Bd. CVI. 1859.

(6) G. Wertheim. Annales de chemie et de physique. Tom. 50. 1857.

the angle of torsion into two parts, i.e. the elastic part and the set part; he disregards, however, the elastic yielding.

The experiments on torsion thus far referred to were made on specimens, which were almost wholly metallic substances. Bevan<sup>(1)</sup> in "Experiments on the Modulus of Torsion" has given a table of the modulus of torsion for different kinds of wood. The strength of stone and mortar was investigated by Bevan<sup>(2)</sup> with glue and by Rondelt<sup>(3)</sup> with mortar: but they rather belong under the category of adherence.

Several distinguished elasticians have mathematically treated the elastic nature of rocks—or rather, of crystals—but the result of their subtle analysis is of little use to the study of geological phenomena. Quite recently, Professor H. Nagaoka<sup>(4)</sup> has published an essay, containing a valuable table of the rigidity modulus of the various rocks, which compose the outer coating of our planet.

The present experiments were undertaken under the professor's kind guidance, for the purpose of extending his investigations. The following paper contains the results of the experiments on torsion, and its principal object is to show how great the *defect of Hooke's law* is and how great *hysteresis* there exists in the relation of torsion to couple. In mathematical part, a *formula for the hysteresis-function* due to the elastic yielding (*Elastische Nachwirkung* or *Weber's Effect*) is deduced. Lastly, as an appendix, the well-known wide difference between the velocities of the tremors and those of the principal shocks in an earthquake is explained, as an effect of the elastic yielding of the rocks through which the seismic waves are propagated.

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(1) Bevan. Phil. Transactions. 1829.

(2) Bevan. Phil. Magazine. Vol. LXVIII., 1826.

(3) Rondelt. Traité théorique et pratique de l'Art de Batir. 1830-32.

(4) H. Nagaoka. E. C. of Rocks and the velocity of the Seismic Waves. The Pub. of the E. I. C. in Foreign Languages. No. 4. 1900. Phil. Mag. 1900.

## ARRANGEMENT AND TWISTING APPARATUS.

The arrangement for the experiment was, on the whole, one and the same as that used by Professor H. Nagaoka,<sup>(1)</sup> but with such adaptations as were necessary to make the stress cyclical. Preliminary experiments, as the professor noted in his publication above cited, showed a great defect of Hooke's law and the existence of remarkable hysteresis. Fig. 1, Pl. I., shows the general features of the relation of stress to strain in a piece of sandstone. Thus, it will be obvious that, in the ordinary sense of the term, it is nonsense to speak of the modulus of rigidity of rocks. The value suggested by the mathematical theory as the limiting one is to take the tangent of the angle which the tangent at the origin to the stress-strain curve makes with the strain axis. But, it is extremely difficult to determine this angle, because the experimental error due to the non-delacy of the apparatus is greatest where the stress is vanishingly small. Possibly sound-experiments might be the best method of ascertaining this limiting value. The result deduced from such infinitely small strains as occur in sound vibrations is no doubt of great value as regards the elastic property of matter ; but it must be far from what we have to consider in the study of the geological phenomena and seismic waves.

The chief features of my improvements of the arrangement were ;—firstly, to twist the specimen cyclically with increasing and decreasing couple *passing through zero continuously* ; secondly, to get rid of the influence of the friction between the parts of the instrument ; and thirdly, to eliminate any external disturbance such as the yielding of the scale-support or minute displacements of the telescope.

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(1) H. Nagaoka. The Pub. of the Earthquake Invest. Committee in Foreign Languages. No. 4. 1909

Figures in Pl. II. show the twisting apparatus thus improved, together with a rough sketch of the whole arrangement. Here it is only necessary to remark that any couple whatever, positive or negative, could be produced without any increase of load to be supported by the knife-edge.

*The order of observation* was as follows :—

1. To begin with, a specimen, whose dimensions were nearly  $1 \times 1 \times 15$  centimetres, was firmly clamped in horizontal position and at right angles to the plane of the pulleys.
2. The directions of the two mirrors attached to the specimen were so adjusted that the two images of the vertical scale, whose distance from the specimen was 2.716 metres, stood side by side within the field of one and the same telescope, mounted on a tripod.
3. Equal weights, each  $\frac{1}{2} M_0$ , were put on the pans  $Q_1$  and  $Q_2$ , which, as a matter of course, gave no couple to the specimen.
4. Zero-readings were taken firstly for the right image which was reflected from the mirror attached close to the fixed end of the specimen, then as fast as I could for the left image which corresponded to the free end.
5. A definite number of pieces, which constituted the weight  $\frac{1}{2} M_0$ , say  $\frac{1}{2} M$  were taken off from one of the pans and put on the other. The resulting couple was obviously equal to  $Mgr$ , if  $r$  represent the radius of the twisting pully and  $g$  the value of gravity. A time-record corresponding to this transposition of weight was taken.
6. After a certain definite time, the readings were taken for both images, as in the case of zero-readings.
7. Second transposition of weight; the time recorded; scale



readings taken : and so on till a definite amount of couple was reached.

8. Then, the weight was transposed in the opposite way so that the couple diminished gradually and ultimately became oppositely directed. In this way, a series of observations was made to complete the cycle many times.
9. From the difference of the deviations of the two images, the amount of twist due to the corresponding weight difference was calculated. One mm. of scale division  $= 1.845 \times 10^{-4}$  radian. One gram of mass  $= 6.712 \times 10^3$  e.g.s. unit of couple.

Thus, it will be easily seen that the result of observation was at no time affected by any external disturbance such as the yielding of the scale-support, or minute displacements of the telescope, or flexure of the floor on which the twisting apparatus rested. One instance is given in Pl. III. for the case of a piece of clay slate. As might be expected, the irregularity of the course of the curve A is enormous, while the course of the curve B is quite free from it.

Here it is necessary to explain why, in the third operation above mentioned, I put a superfluous weight  $\frac{1}{2} M_0$  on the pans giving no couple. When the two weights, whose respective masses are  $m_1$  and  $m_2$ , are put on the pans  $Q_1$  and  $Q_2$  respectively, the resulting couple is given by

$$C = [\{m_1 - m_2\} \mp \sigma \{m_1 + m_2\}] \text{ rg.}$$

the upper or the lower of the double sign being selected according as  $\{m_1 - m_2\}$  is increasing or decreasing ; where  $\sigma$  is a numerical coefficient depending on a dissipation of couple due to the imperfectness of the arrangement ; e.g. friction of the pulley, imperfect flexibility and extensibility of the strings. For future reference,  $m_1 - m_2 = M$  and  $m_1 + m_2 = M_0$  will be called the *Effective Mass* and the *Resisting Mass* respectively. Thus

$$\mathfrak{C} = \{M \mp \sigma M_0\}rg = Mrg \mp \text{constant}, \quad \text{provided } -M_0 < M < +M_0,$$

whence  $\frac{d\mathfrak{C}}{dM} = rg = \text{constant} = 6.712 \times 10^3$  per gram.

Or graphically, the relation between  $M$  and  $\mathfrak{C}$  may be expressed by a narrow parallelogram whose shorter sides are parallel to the axis of  $M$  and *the angle contained by the adjacent sides is independent of the imperfection of the apparatus.* The value of  $\sigma$  determined by direct experiments is :

from the first experiment,  $\sigma_1 = 0.0128$  ;

from the second experiment,  $\sigma_2 = 0.0132$  ;

mean of the two,  $\sigma = 0.0125$  ;

Thus for instance, if the resisting mass be two kilograms, the couple due to the effective mass of  $N$  grams is

either  $\mathfrak{C}_i = \{N - 25\}rg$  , for the increasing couple

or  $\mathfrak{C}_d = \{N + 25\}rg$  , for the decreasing couple.

## GENERAL INVESTIGATION OF THE STRESS-STRAIN RELATION.

Two specimens, serpentine and pyroxenite, whose limits of elasticity seemed to be comparatively wide, were tested by a series of cycles of positive and negative couples which gradually increased in their absolute amount.

Half the difference between the maximum and minimum couples in a cyclical process of the twisting and untwisting will be called the *Amplitude* of the cycle. Half the sum of these two couples will be called the *Centre* of the cycle. For instance, if the couple varies cyclically between  $j + \theta$  and  $j - \theta$ , then  $\theta$  and  $j$  are called the amplitude and the centre of the cycle respectively.

In the present experiments, the centre being at origin i.e.  $j = 0$ ,

the specimens were twisted to and fro cyclically up to the amplitude  $\theta$  given below :—

$$\theta = 2.68 \quad ; \quad = 6.71 \quad ; \quad = 10.07 \quad ; \quad = 16.11 \quad ; \quad = 20.14 \quad \times 10^6 \text{ c.g.s. units.}$$

The result of the experiments is plotted in Pl. IV. It will be seen, at a glance, that

1. If the curve be divided into several sections at the positions where the variation of couple changes its sign, each section, except the one which starts from the origin, will be approximately straight, provided a comparatively small portion immediately after the turning point is left out of consideration.
2. None of the sections except the one which starts from the origin, pass through the origin. Each section for which the variation of couple is a positive, or on-curve, lies below the origin, i.e. it passes through the fourth quadrant : while each section for which the variation is a negative, or off-curve, passes through the second quadrant.
3. Suppose a straight line to be drawn coinciding as nearly as possible with each section. Of these representatives, that which represents the section which belongs to a cycle of greater amplitude lies further from the origin.
4. That which lies further from the origin makes a greater angle with the axis of couple.

Of the above facts, the first shows that Hooke's law is approximately fulfilled, provided the change of couple always takes place in *one direction* only ; and that there must be a certain disturbing cause, prevailing especially in the neighbourhood of the starting point and at the turning point of the course. The second shows that there is certain dissipation of energy for each cycle, due either to the imperfect elasticity of the twisted rocks or to the imperfection of the twisting apparatus. Observe that the latter is a constant. The

third teaches us that the dissipation above stated increases more and more when the amplitude of the cycle becomes greater and greater. This increase of the dissipation must necessarily be due to the imperfect elasticity of the specimen. The fourth means that the specimen becomes less and less rigid when it is twisted further and further. Thus, the ordinary conception of the modulus of rigidity is necessarily vague and uncertain. In future, the *actual resistance* to the deformation in any state whatever, be it elastic or plastic at that state, will be taken as the measure of rigidity at that state. Hence: *The Rigidity-Modulus of a substance in a given state is measured by the increase of stress required to give a unit increase of deformation to the substance in that state*: i.e. the trigonometrical tangent of the angle which the tangent to the stress-strain curve at a point corresponding to that state, makes with the strain axis.

The following numerical calculations show the above facts quantitatively:—The equation of the representative straight line is either  $\alpha + \beta M = \delta$  or  $\beta\{M - \gamma\} = \delta$ ; where  $M$  and  $\delta$  being the effective mass and the corresponding deflection of the image respectively,  $\alpha$  is proportional to the residual twist surviving the couple which is proportional to  $M$ , and  $\beta$  is inversely proportional to the rigidity-modulus of the specimen at that state: while  $\gamma$  is the effective mass which is required to bring the specimen into the state of no torsion. The couple required to detort the specimen is, as G. Wiedemann<sup>(1)</sup> noted in his experiment on metallic wire, obviously less than the couple which produced that tort. The following table giving the relation between  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\theta$  proves the above statements.

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(1) G. Wiedemann, Pogg. Annalen. Bd. CVI. 1859.

TABLE I.

Specimen.	No. 8 <sub>2</sub> . Serpentine from Chichiba.			No. 32 <sub>1</sub> . Pyroxenite from Gumma.		
Constant	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
Amplitude						
0.0	$\mp 0.01105$	0.255	$\pm 0.0434$	$\mp 0.0074$	0.249	$\pm 0.0390$
0.4	$\mp 0.0295$	0.424	$\pm 0.0691$	$\mp 0.0322$	0.428	$\pm 0.0752$
1.0	$\mp 0.0529$	0.485	$\pm 0.1091$	$\mp 0.0538$	0.497	$\pm 0.1082$
1.5	$\mp 0.0633$	0.508	$\pm 0.1254$	$\mp 0.0873$	0.504	$\pm 0.1732$
2.4	$\mp 0.0987$	0.513	$\pm 0.1924$	$\mp 0.1229$	0.529	$\pm 0.2324$
3.0	$\mp 0.1212$	0.527	$\pm 0.2300$	(M <sub>0</sub> = 3300 grams)		

Here, of the double sign, the upper or the lower must be selected according as the required twist corresponds to the increasing or decreasing state of the effective mass.

Now plotting the value of  $\gamma$  against the value of  $\theta$ , as is shown in Fig. 9 Pl. V., we see that  $\gamma$  may be expressed as a linear function of  $\theta$ , so that

$$\gamma = \sigma M_0 + h \theta$$

where  $h$  is a constant depending on the imperfect elasticity of the specimen. Numerical values of  $\sigma$  and  $h$  obtained from the above experiments are :—

$$\text{No. 8}_2. \quad \sigma_1 = 0.0128 \quad , \quad h_1 = 0.0817$$

$$\text{No. 32}_1. \quad \sigma_2 = 0.0132 \quad , \quad h_2 = 0.0619$$

The values of  $\sigma_1$  and  $\sigma_2$  which must be equal to each other, coincide tolerably well within the error of observation. The difference of plasticity of several rocks will be indicated by the relative values of the constant  $h$ .

## THE DOUBLY INDEFINITE CHARACTER OF THE MODULUS OF RIGIDITY.

From the experiments, some of which are graphically shown in Pls. IV. and VI., we may easily conclude that

1. When the maximum amount of stress, to which the specimen has just been subjected, is given, the modulus of rigidity is a function of the stress actually acting upon it.
2. When the stress acting upon it is given, the modulus of rigidity is a function of the maximum amount of the stress to which the specimen has just been subjected.

Of these two, the first expresses simply that Hooke's law is defective, while the second shows the existence of torsional hysteresis. One numerical example is given in the following table to show how the modulus of rigidity, even in the limiting case of a vanishingly small stress, varies with the magnitude of the stress just previously applied.

TABLE II.

Modulus of rigidity, taken at the state of a vanishingly small stress.					
Previous couple (Arbit. unit)	1	30	75	115	185
Specimen					
Serpentine	$5.22 \times 10^{11}$	3.14	2.74	2.62	2.59
Pyroxenite	$4.90 \times 10^{11}$	2.84	2.45	2.44	2.30

The relation is also graphically shown in Fig. 11<sub>a</sub>, Pl. V.

Here, it may be necessary to remark that, even when Hooke's law is approximately fulfilled, the factor of proportionality may entirely depend on its previous history. To give one instance, in the result of the experiment shown in Figs. 12 and 13, Pl. VII., there is little or no objection to assuming Hooke's law, provided each series of observations, be it either in the case of an on or an off curve, is considered independently from the other. Moreover, the factor of proportionality for the on-curve is nearly equal to that for the corresponding off-curve. It, however, never remains the same for the two different series.

The numerical values are :— {Specimen No. 4<sub>2</sub>. Sandstone}.

$$\mu_1 = 0.72 \times 10^{10} \quad ; \quad \mu_2 = 1.25 \times 10^{10}$$

There is no reason to reject either of them, since they were measured in one and the same manner under equal surrounding conditions. Nothing but the difference of previous history can account for the cause of such an ambiguity in the modulus of rigidity.

### YIELDING AND RECOVERY FROM THE YIELDING.

Attention was first drawn by Weber<sup>(1)</sup> to this subject. He called it "*Prolongatio vel contractio secundaria*." It requires a certain duration as well as magnitude of stress ; it disappears if the stress be removed for a certain period. Ignace Giulio<sup>(2)</sup>, in his experiments on torsion of metallic wire, recognized also the existence of both the yielding and the recovery ; but as he could not find any quantitative relation, so he concluded his memoir with the following question :— "*Quelle est la fonction de la tension et du temps suivant laquelle ces altérations se produisent et disparaissent ?*"

YIELDING :—In most rocks, the yielding is considerable. Indeed, it is doubtful whether there is any limit to the elastic yielding of certain rocks, at least, when the twisting couple is sufficiently great. In the following experiments, equal weights were put on the two pans, which gave no couple, and the readings corresponding to that state were taken. At a known instant, a definite amount of weight was transported from one pan to the other. Then the readings were taken from instant to instant. The results of the experiments are shown in Fig. 14, in Pl. VIII. In these two experiments, the effective mass was the same but with different resisting masses.

(1) Weber. W. Weber's Werke: her. v. d. Konig. Gesel. d. Wiss. zu Göttingen. Bd. I. pp. 475-488.

(2) Ignace Giulio. Memorie della reale Accademia delle Scienze di Torino. Serie II. Tom. IV, 1842.

The influence of the different magnitudes of the constant couple (the resisting mass being the same) upon the yielding was then examined. In successive experiments, the constant couples were in the ratio of 3 : 5 : 7 : 9 : 11 : 13 : 15. The curves in Pl. IX. show the result. As a matter of course, all curves are of similar form, but there exists the remarkable difference that of any two curves, the one whose couple was the smaller, approaches to horizontality more quickly than the other. Here it must be observed that the absolute amount of twist is not known, since the so-called zero-reading is nothing but the reading which corresponds, as the case may be, to a certain unknown twisting couple lying between  $+M_0\sigma_{gr}$  and  $-M_0\sigma_{gr}$ . In other words, all curves in Pl. IX. are not referred to one and the same origin of coordinates.

RATE OF THE YIELDING :—From the values of the twist and of the corresponding time, the rate of the yielding may be calculated by the formula

$$\frac{\Delta\tau}{\Delta t} = \frac{\tau_{(t'')} - \tau_{(t')}}{t'' - t'}$$

where  $\tau_{(t)}$  represents the amount of twist at the instant  $t$ . Plotting the result, obtained from eight observations, as shown in Fig. 16, Pl. X., we may, at once, perceive that the general relation between the rate of yielding and the time-element much resembles something like a rectangular hyperbola. To test whether this is true or not, instead of  $\frac{\Delta\tau}{\Delta t}$  and  $t$  themselves, their logarithms are plotted in Fig. 17 on the same plate. The most probable curve and also the simplest at the same time, would be a straight line. One straight line, whose equation is

$$\log \frac{\Delta\tau}{\Delta t} + \log t = \log \frac{1}{10}$$



is drawn in the figure. Then, the equation of the corresponding hyperbola is

$$t \frac{\Delta \tau}{\Delta t} = -\frac{1}{10}$$

which is also traced in the corresponding figure. {Eight of such straight lines and hyperbolas should be drawn in the figures to correspond to all the points dotted there.}

Assuming that the relation between the rate of yielding and the time-element is given by the above equation, we may write.

$$d\tau = k \frac{dt}{t}$$

which when integrated becomes

$$\tau = k \log t + \text{constant.}$$

Let the value of  $\tau$  at the time  $t=1$  be represented by  $\tau_0$ , and we have

$$\eta = \tau - \tau_0 = k \log t$$

as the value of the twist due to the yielding, provided the yielding is counted after the lapse of a unit time. In Fig. 18, Pl. IX., the curves are traced for two different values of  $k$ . Here it must be observed that the constant  $k$  must depend on the amount of the constant couple as well as on the nature of the rocks. As C. F. Dietzel<sup>(1)</sup> found in his experiments on vulcanized caoutchouc the yielding is, most probably, proportional to the stress, so that we may put

$$k = \nu. \mathfrak{C}$$

or 
$$\eta = \nu. \mathfrak{C}. \log t.$$

where  $\nu$  is a constant depending on the nature of the rock.

Now it may be doubted whether the yielding can actually proceed without limit in time. To ascertain this point, a specimen was subjected under a constant couple for a long time, and then the time variation of its twist was observed. The result is shown in

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(1) C. F. Dietzel. Polytechnisches Centralblatt: Jahrgang 1857. Leipzig.

Figs. 19-22, Pl. XI., which shows steady increase of the twist even after the lapse of many thousands of minutes.

RECOVERY FROM THE YIELDING :—To examine whether the yielding above investigated is elastic or permanent, a specimen was subjected under a constant couple during one hundred and sixty-seven hours, and then it was suddenly released from the couple. The amount of residual was observed from instant to instant with the corresponding time-record. The result is shown in Figs. 23 and 24 in Pl. VIII. This curve of recovery resembles, as a whole, that of yielding.

Again, to investigate the influence of the recovery on the cycles, a specimen, which had been subjected under a constant couple during three hundred and six and a half hours, was twisted to and fro cyclically. Gradual recovery, as is shown in Fig. 25, Pl. XII., may be traced along the whole cycle. Comparing this with that drawn in Pl. VI., both of which were treated in one and the same manner as regards the cyclic process, the effect of the recovery will be more clearly understood. Fig. 26 in Pl. XIII., shows the result of the next experiment conducted on the same specimen in a similar manner. Here, the form of curve, as a whole, has a centre of symmetry coinciding with that of the cyclic process. No possible explanation for this non-coincidence of the last two curves can be found but that, in the first case, in which the specimen had been kept under the couple during very long time, the total yielding having been very great, the specimen had a greater tendency than in the other case to recover from the yielding when the couple was withdrawn.

## THE HYSTERESIS FUNCTION.

From what has been explained in the foregoing pages, we see

that the strain produced by the shearing stress is of a very complicated nature. Though the greater part of the strain occurs almost instantaneously, the total amount of it gradually increases with time : i.e. say  $S=S_0+S_t$ . When the couple is removed, the greater part disappears instantaneously and the remaining part diminishes gradually, and the limiting value for infinite time is generally supposed not to be zero. Thus we have  $S=S'_0+S'_t+S_r$ . The suffixes 0 and  $t$  mean that the strain requires no time and a certain time respectively to appear or disappear, while  $r$  means that it remains for an infinite time. These facts have long been noticed by many experimentalists, as cited in the introduction above. Several distinguished elasticians have endeavoured to establish a relation between these different kinds of strains.

Since there is no reason for assuming  $S_0=S'_0$  and also as  $S'_t$  can not be equal to  $S_t$  unless  $S_r$  is zero, the general expression for the strain must be of a form

$$S=S_{00}+S_{0t}+S_{0r}+S_{t0}+S_{tt}+S_{tr}$$

so that  $S_0=S_{00}+S_{0t}+S_{0r}$  ;  $S'_0=S_{00}+S_{t0}$  ;  $S_t=S_{t0}+S_{tt}+S_{tr}$  ;

$$S'_t=S_{0t}+S_{tt} \text{ ; and } S_r=S_{0r}+S_{tr}.$$

To establish a complete relation between stress, strain and time, we must find a relation between the stress and each term of the strain above mentioned.

The simplest is the case where all the terms except the first are negligibly small. Such a body is generally said to be perfectly elastic. Within proper limits, which are called the limits of elasticity, this is the case for most hard solids. As regards the relation between stress and strain under this condition, Hooke's investigation was most satisfactory and the result expressed in the law, well known by his name—Hooke's law—is so closely associated with perfect elasticity

that some writers have taken "*defect of Hooke's Law*" to mean "*defect of perfect elasticity*," which is obviously absurd.

When other terms are not negligible, the stress-strain relation is so complicated that we have not yet any established law, notwithstanding the utmost endeavours of several distinguished elasticians and engineers. A. F. W. Brix<sup>(1)</sup> recognised only two terms  $S_{00}$  which followed Hooke's law and  $S_{0r}$ , for which he could discover no law. G. Wertheim<sup>(2)</sup> divided the angle of torsion into two parts which correspond to  $S_0$  and  $S_r$  respectively, but he disregarded the terms corresponding to  $S_t$  and  $S'_t$ . W. Wundt<sup>(3)</sup> concluded that  $S_t$  and not  $S_{00}$ , was proportional to the stress that produced it; but reached no definite conclusion as to the term  $S_t$  or  $S'_t$ .

A. W. Volkmann<sup>(4)</sup> found for silk and nerve, the stress-strain relation to be *hyperbolic*, but for muscle to be *elliptic*. He thought this relation something peculiar to organic bodies. In F. E. Neumann's paper<sup>(5)</sup>, we find a consideration of *set* which literally corresponds to the term  $S_r$ . His conclusion is that the principal sets can be taken as linear functions of the principal elastic strain. More recently, Voigt<sup>(6)</sup> discussed the relation between  $S_{00}$  and  $S_r$  for the case of bending; while James Muir<sup>(7)</sup> experimented on the *recovery from overstrain* which corresponds to  $S'_t$ , but he arrived at no quantitative relation.

After all, it is no easy matter to state any exact physical relation between stress, strain and time-element. In the following pages, the

(1) A. F. W. Brix. Abhandlungen über die Cohäsions- und Elasticitäts-Verhältnisse einiger.....Eisendrähte.....; Berlin, 1837.

(2) G. Wertheim. Annale de chemie et de physique. Tom. 50. 1857.

(3) W. Wundt. Archiv für Anatomie, Physiologie und Wiss. Medicin. Jahrgang 1857.

(4) A. W. Volkmann. Archiv für A, P, u. s. w. herausgegeben v. C. B. Reichert und E. de Bois-Reymond. Bd. I. 1859.

(5) F. E. Neumann. Vorlesungen über die Theorie der Elasticität der festen Körper und des Lichtäthers. 1885.

(6) Voigt. Untersuchung der Elasticitätsverhältnisse des Steinhalzes. Leipzig. 1874.

(7) J. Muir. Phil. Transactions. 1900.

yielding appears necessarily to be *elastic*; or recovery is complete if the stress be removed for an *infinite time*. Thus, *absolute set* is disregarded here. It may have, no doubt, more or less magnitude;—in magnetic hysteresis, indeed, we recognize its existence as very common. I doubt, however, whether it is really as great as it is repeatedly reported to be in the writings of experimentalists. What many experimentalists have called *set* appears to have been in greater part *not absolute set but elastic yielding*. For instance, when E. Chevandier and G. Wertheim<sup>(1)</sup> considered the strain to consist of two parts, i.e. an elastic part and permanent part, or when G. Wiedeman<sup>(2)</sup> speaks of the temporary torsion and the torsional sets, the elastic yielding obviously comes within the latter category. To cite the best example, Ignace Giulio<sup>(3)</sup> whose experimental discussion of set is very interesting, says himself: “On voit encore que ce que j’ai nommé jusqu’ici *Allongement Permanent*..... *disparaît en grande partie après un temps suffisamment long*.....”

The following pages contain some mathematical investigations concerning the *Hysteresis Function* due to the elastic yielding. Assume that the strain consists of two parts of which the first follows Hooke’s law, being independent of time, and the second, though it is also proportional to the stress, depends on a time-element in a manner given by the relation established in the former experiments. Then an interesting formula for the hysteresis function may be deduced, from which the expressions for the amount of yielding as well as for the amount of residual after any number of reversals of twisting and untwisting, and all other properties of the torsional hysteresis follow at once.

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(1) E. Chevandier and G. Wertheim. *Mémoire sur les propriétés mécaniques du bois*. 1848.

(2) G. Wiedemann. *Pogg. Annalen*. Bd. CVI. 1859.

(3) I. Giulio. *Memorie della reale Accademia delle Scienze di Torino*. Serie II, Tom. IV. 1842.

Let the principle of superposition be assumed to hold good for the case of yielding, and take for granted the following relation, no matter how or from what hypothesis it may have been obtained,

$$\eta = k \log t. * \quad (1).$$

To simplify the matter, let us suppose that a definite amount of couple begins to act at the origin of time and remains acting for an infinite time; and also that after each unit of time—in my experiments it was one minute—the couple is increased by the same amount. Then, the total amount of the yielding at the instant  $T=p$  is given by

$$\eta = \eta_p + \eta_{p-1} + \dots + \eta_2 + \eta_1 = k \log I\{p+1\} \quad (2).$$

where  $I$  is a well-known symbol for Gamma-function.

If a negative couple were to act at the instant  $T=p+1$  and afterwards, increasing in its absolute amount step by step like the positive couple, the yielding due to this negative couple at the instant  $T=p+r$  would evidently be

$$\eta = -k \log I\{r+1\}$$

Hence, if the couple increases for the first  $p$  minutes and then remains constant for the following  $r$  minutes, the yielding at the instant  $T=p+r$  is

$$\eta = k \log I\{p+r+1\} - k \log I\{r+1\} = k \log \frac{I\{p+r+1\}}{I\{r+1\}}. \quad (3).$$

Again, if the couple after an increase for the first  $p$  minutes, remains constant for the next  $r$  minutes, and then decreases step by step during last  $n$  minutes, the yielding at the instant  $T=p+r+n$ , as it may easily be seen, is given by

\* In Page 15, we had the formula  $\eta = \tau - \tau_0 = k \log t$ , where  $\tau_0$  is the value of  $\tau$  at the time  $t=1$ , so that the expression for the yielding i.e.  $\eta = k \log t$  holds good only for  $t > 1$ . When the present paper is under the press, it is kindly noted by Mr. S. Sano, that it is better to take a form  $\eta = k \log \frac{t+\theta}{\theta}$ , where  $\theta$  is a constant, than to take the form given in the text. It is very good of him to have given me so much of other valuable remarks. The author would like to thank him for all his kindness.

$$\tau = k \log \frac{I\{p+r+n+1\}}{I\{r+n+1\}I\{n+1\}}. \quad (4).$$

Lastly, if the couple remains constant after this moment, then the yielding at the instant  $T=p+r+n+t$  is given by

$$\tau = k \log \frac{I\{p+r+n+t+1\}I\{t+1\}}{I\{r+n+t+1\}I\{n+t+1\}}. \quad (5).$$

Proceeding in this way, we may find the value of  $\tau$  after any number of torsional cycles. I give here its general form. Suppose we start from the origin, at the instant  $T=0$ , which corresponds to the neutral state of the specimen, and for the sake of simplicity also suppose that the change of couple takes place by unit amount per unit of time.

1. Increasing the couple step by step we reach a couple  $=I$  at the instant  $T=i_1$ , so that  $I=i_1$ ;

2. for the next  $r_1$  minutes, the couple remains constant to the instant  $T=i_1+r_1$ ;

3. then it decreases step by step and ultimately, going even to the negative direction, becomes equal to  $II$  at the instant  $T=i_1+r_1+i_2$ , so that  $II=i_1-i_2$ ;

4. here the couple remains constant and equal to  $II$ . during the next  $r_2$  minutes;

5. again, the couple increases once more till it becomes equal to  $III$  at the instant  $T=i_1+r_1+i_2+r_2+i_3$ , so that  $III=i_3-i_2+i_1$ ;

etc.            etc.            etc.

where  $I, II, III, \dots, N$  represent certain definite amounts of couple, positive or negative as the case may be. Let  $p$  and  $n$  denote any given stage in the cycle on the increasing or decreasing procedures respectively, and  $t$  the time during which the couple remains constant at the last stage  $p$  or  $n$ ; also let  $\nu$  be the number of reversals of the couple from increasing to decreasing or from decreasing to

increasing, so that  $N$  is the amount of couple in which the  $\nu^{\text{th}}$  reversal occurs.

These premised, we may write the general expression for the hysteresis function as follows :—

If  $\nu$  is even, the amount of yielding,  $\eta_p$ , is given by the expression

$$k \log \frac{\Gamma\{p-N+t+1\} \Gamma\{p-N+r_\nu+t+1\} \left[ \prod_1^{\frac{\nu}{2}} \left[ \Gamma\left\{ \sum_{2\rho-1}^{\nu} (i_\epsilon + r_\epsilon) + p - N + t + 1 \right\} \right] \right] \left[ \prod_1^{\frac{\nu}{2}-1} \left[ \Gamma\left\{ \sum_{2\rho+1}^{\nu} (i_\epsilon + r_\epsilon) + r_{2\rho} + p - N + t + 1 \right\} \right] \right]}{\Gamma\{t+1\} \left[ \prod_1^{\frac{\nu}{2}} \left[ \Gamma\left\{ \sum_{2\rho}^{\nu} (i_\epsilon + r_\epsilon) + p - N + t + 1 \right\} \right] \right] \left[ \prod_1^{\frac{\nu}{2}} \left[ \Gamma\left\{ \sum_{2\rho}^{\nu} (i_\epsilon + r_\epsilon) + r_{2\rho-1} + p - N + t + 1 \right\} \right] \right]} \quad (6).$$

If  $\nu$  is odd, the amount of yielding,  $\eta_n$ , is given by the expression

$$k \log \frac{\Gamma\{t+1\} \left[ \prod_1^{\frac{\nu+1}{2}} \left[ \Gamma\left\{ \sum_{2\rho-1}^{\nu} (i_\epsilon + r_\epsilon) + N - n + t + 1 \right\} \right] \right] \left[ \prod_1^{\frac{\nu-1}{2}} \left[ \Gamma\left\{ \sum_{2\rho+1}^{\nu} (i_\epsilon + r_\epsilon) + r_{2\rho} + N - n + t + 1 \right\} \right] \right]}{\Gamma\{N-n+t+1\} \Gamma\{N-n+r_{\nu-2}+t+1\} \left[ \prod_1^{\frac{\nu-1}{2}} \left[ \Gamma\left\{ \sum_{2\rho}^{\nu} (i_\epsilon + r_\epsilon) + N - n + t + 1 \right\} \right] \right] \left[ \prod_1^{\frac{\nu-1}{2}} \left[ \Gamma\left\{ \sum_{2\rho}^{\nu} (i_\epsilon + r_\epsilon) + r_{2\rho-1} + N - n + t + 1 \right\} \right] \right]} \quad (7).$$

As a particular case, when the twist and untwist occurs  $\lambda$  times cyclically within a constant amplitude  $\mathfrak{A}$ , with origin as centre and the couple not remaining constant at the moment of reversal—i.e.  $r_\rho = 0$ , the amount of yielding at the increasing stage  $p$  is given by

$$\eta_p = k \log \frac{\Gamma\{4(\lambda+1)\mathfrak{A}+p+1\} \left[ \prod_0^{\lambda} \left[ \Gamma\{4(\lambda+1)\mathfrak{A}-(4\rho+3)\mathfrak{A}+p+1\} \right] \right]^2}{\left[ \prod_0^{\lambda} \left[ \Gamma\{4(\lambda+1)\mathfrak{A}-(4\rho+1)\mathfrak{A}+p+1\} \right] \right]^2} \quad (8).$$



Let us now investigate some general properties of this hysteresis function in the following pages ;—To begin with, it is necessary to remark that the strain corresponding to any stress is here supposed to consist of two terms, of which the principal term is simply proportional to the actual stress while the other is given by the hysteresis function,  $\tau$  ; thus

$$\tau = \tau_0 + \tau. \quad (9).$$

Let the specimen be freed from any external couple after it has been once acted upon by a couple whose amount is given by  $p$ , so that in the equation (4)  $n=p$ , and then let it be again acted upon by a couple. The yielding *apparently due to unit couple*, no matter whether it be positive or negative, is given by

$$\left\{ -\frac{\Delta \tau}{\Delta p} \right\}_{p=n} = k \log \frac{\{2p+r+1\}}{\{p+r+1\}\{p+1\}} = -\tau_2 \quad \text{say} \quad (10).$$

which is always negative. Now, if the newly applied couple be negative, the principal term due to this negative couple is necessarily negative ; let it be  $-\tau_1$  so that the *increase of twist* apparently due to this negative unit couple is

$$\tau_n = -\{\tau_1 + \tau_2\} \quad (11).$$

On the other hand, if it be positive, the principal term is also positive and, by Hooke's law, equal to  $+\tau_1$  ; so that the *increase of twist* due to this positive couple is

$$\tau_p = \tau_1 - \tau_2 \quad (12).$$

Thus, the absolute value of  $\tau_n$  being greater than that of  $\tau_p$ , we have following interesting result :

PROPOSITION I. *If after withdrawing the whole couple applied to a piece of rock, we begin to reapply it, the specimen must apparently be more rigid in one direction than in the other.*

In the equation (5) put  $p=n$ , and we have

$$\sigma = k \log \frac{\Gamma\{2p+r+t+1\} \Gamma\{t+1\}}{\Gamma\{p+r+t+1\} \Gamma\{p+t+1\}} \quad (13).$$

which is the *expression for the residual* surviving the couple, since in this case  $n$  being equal to  $p$  the specimen is free from any external couple.

Taking the difference of  $\sigma$  for two consecutive values of  $t$ , we have

$$\frac{\Delta\sigma}{\Delta t} = k \log \frac{\{2p+r+t+1\}\{t+1\}}{\{p+r+t+1\}\{p+t+1\}} < 0 \quad (14).$$

which is evidently negative, because any rectangle is smaller than a square when their periphery is given. Also, the limiting value of  $\sigma$  as well as of  $\frac{\Delta\sigma}{\Delta t}$  is zero for  $t=\infty$ . Thus we have.

PROPOSITION II. *The residual diminishes with the lapse of time and ultimately disappears wholly after an infinite time. Consequently, the yielding is elastic, and recovers wholly if the couple is removed for an infinite duration.*

The differential for the unit increase of  $r$  is

$$\frac{\Delta\sigma}{\Delta r} = k \log \frac{\{2p+r+t+1\}}{\{p+r+t+1\}} > 0 \quad (15).$$

which is positive since the fraction is greater than unity; but the second differential being negative. We have.

PROPOSITION III. *The residual—so-called set—increases with the increase of the time during which the couple acted on the specimen.*

Here it must be remarked that the *expression for the recovery* may be deduced from that for the residual. It is given by

$$\rho = k \log \frac{I\{2p+r+1\}I\{p+r+t+1\}I\{p+t+1\}}{I\{p+r+1\}I\{p+1\}I\{2p+r+t+1\}I\{t+1\}} \quad (16).$$

where  $r$  expresses the time-element during which the specimen remained acted by a constant couple  $p$ . Thus it is evident that the curve of recovery is a little different from that of yielding whose

equation is (1). For a particular case,  $p=10$  and  $r=0$ , the curve of recovery is traced in Fig. 27, Pl. VIII.

Again, from the equation (8), the difference between the yieldings at the two consecutive stages  $p$  and  $p+1$  is

$$\frac{\Delta \gamma}{\Delta p} = k \log \frac{\left\{ 4(\lambda+1)\mathfrak{A}(p+1) \right\} \prod_0^{\lambda} \left[ 4(\lambda+1)\mathfrak{A} - (4\rho+3)\mathfrak{A}(p+1) \right]^2}{\prod_0^{\lambda} \left[ 4(\lambda+1)\mathfrak{A} - (4\rho+1)\mathfrak{A}(p+1) \right]^2} = k \log \varepsilon \quad \text{say.} \quad (17).$$

Putting  $p=-\mathfrak{A}$ , the expression for  $\varepsilon$  may be written in a form, if we write  $\mathfrak{B}$  for  $4(\lambda+1)\mathfrak{A}$ ,

$$\varepsilon = - \frac{\{\mathfrak{B}+1-\mathfrak{A}\}\{\mathfrak{B}+1-4\mathfrak{A}\}}{\{\mathfrak{B}+1-2\mathfrak{A}\}^2} - \frac{\{\mathfrak{B}+1-4\mathfrak{A}\}\{\mathfrak{B}+1-8\mathfrak{A}\}}{\{\mathfrak{B}+1-6\mathfrak{A}\}^2} - \dots - \frac{\{1+4\mathfrak{A}\}}{\{1+2\mathfrak{A}\}^2} < 1$$

which is less than unity since each group of the component fractions is less than unity; whence for this value of  $p$ ,

$$\left\{ \frac{\Delta \gamma}{\Delta p} \right\}_{p=-\mathfrak{A}} < 0. \quad (18).$$

Putting  $p=\mathfrak{A}$ , it may also be written in a form

$$\varepsilon = \frac{\{\mathfrak{B}+1+\mathfrak{A}\}}{\{\mathfrak{B}+1\}} \cdot \frac{\{\mathfrak{B}+1-2\mathfrak{A}\}^2}{\{\mathfrak{B}+1\}\{\mathfrak{B}+1-4\mathfrak{A}\}} - \dots - \frac{\{1+6\mathfrak{A}\}^2}{\{1+8\mathfrak{A}\}\{1+4\mathfrak{A}\}} - \frac{\{1+2\mathfrak{A}\}^2}{\{1+4\mathfrak{A}\}} > 1$$

which is greater than unity, so that for this value of  $p$  we have

$$\left\{ \frac{\Delta \gamma}{\Delta p} \right\}_{p=\mathfrak{A}} > 0 \quad (18').$$

From what has been proved just above, (18) and (18'), we may infer

PROPOSITION IV. *When a specimen is twisted cyclically, the twist may increase notwithstanding the decrease of the applied couple, and vice versa.*

The equation (17) may be written in a form, if we put  $\mathfrak{R}=4(\lambda+1)\mathfrak{A}(p+1)$  for the sake of brevity,

$$\frac{\Delta \gamma}{\Delta p} = k \log \frac{\mathfrak{R}\{\mathfrak{R}-3\mathfrak{A}\}^2 \dots \{p+1+\mathfrak{A}\}^2}{\{\mathfrak{R}-\mathfrak{A}\}^2 \{\mathfrak{R}-5\mathfrak{A}\}^2 \dots \{p+1+3\mathfrak{A}\}^2}$$

whose differential with respect to the amplitude  $\mathfrak{A}$  is

$$\frac{\Delta^2 \eta}{\Delta \mathfrak{A} \Delta p} = k \log \left[ \frac{\{\mathfrak{N} + 4(\lambda + 1)\} \{\mathfrak{N} - \mathfrak{A}\}^2 \{\mathfrak{N} + 4(\lambda + 1) - 3(\mathfrak{A} + 1)\}^2 \dots \dots}{\mathfrak{N} \{\mathfrak{N} + 4(\lambda + 1) - (\mathfrak{A} + 1)\}^2 \{\mathfrak{N} - 3\mathfrak{A}\}^2 \dots \dots \dots} \right. \\ \left. \frac{\dots \{p + 1 + 3\mathfrak{A}\}^2 \{p + 1 + \mathfrak{A} + 1\}^2}{\dots \{p + 1 + 3(\mathfrak{A} + 1)\}^2 \{p + 1 + \mathfrak{A}\}^2} \right] > 0 \quad (19).$$

which is always positive since we have

$$\frac{\mathfrak{N} + 4(\lambda + 1)}{\mathfrak{N}} > 1 ;$$

$$\frac{\{\mathfrak{N} - \mathfrak{A}\} \{\mathfrak{N} + 4(\lambda + 1) - 3(\mathfrak{A} + 1)\}}{\{\mathfrak{N} + 4(\lambda + 1) - (\mathfrak{A} + 1)\} \{\mathfrak{N} - 3\mathfrak{A}\}} = 1 + \frac{6\mathfrak{A} - (p + 1)}{\{\mathfrak{N} - \mathfrak{A} + 4\lambda + 3\} \{\mathfrak{N} - 3\mathfrak{A}\}} > 1 ;$$

etc. etc.

PROPOSITION V. *When the centre of cycle is fixed, the hysteresis curve at any stage  $p$  after  $\lambda$  cycles becomes more and more steep when the amplitude of the cycle becomes greater and greater.*

Let the number of cycles be increased from  $\lambda$  to  $\lambda + 1$ , then we have

$$\frac{\Delta^2 \eta}{\Delta \lambda \Delta p} = k \log \frac{\{(4\lambda + 6)\mathfrak{A} + p + 1\} \{[(4\lambda + 6)\mathfrak{A} + p + 1]^2 - 3\mathfrak{A}^2\} + 2\mathfrak{A}^3}{\{(4\lambda + 6)\mathfrak{A} + p + 1\} \{[(4\lambda + 6)\mathfrak{A} + p + 1]^2 - 3\mathfrak{A}^2\} - 2\mathfrak{A}^3} > 0 \quad (20).$$

which is necessarily positive. Again take a further differential :—

$$\frac{\Delta^3 \eta}{\{\Delta \lambda\}^2 \Delta p} = k \log \frac{\{\mathfrak{N}^2 + 8\mathfrak{A}\mathfrak{N}\} \{\mathfrak{N}^2 + 8\mathfrak{A}\mathfrak{N} + 15\mathfrak{A}^2\}^2}{\{\mathfrak{N}^2 + 8\mathfrak{A}\mathfrak{N} + 7\mathfrak{A}^2\}^2 \{\mathfrak{N}^2 + 8\mathfrak{A}\mathfrak{N} + 16\mathfrak{A}^2\}^2} < 0 \quad (21).$$

which is evidently negative.

From what has been just proved, (20) and (21), follows

PROPOSITION VI. *Provided the centre of cycle is fixed at origin, the hysteresis curve becomes more and more steep when the cycle is repeated over and over again and the curve asymptotically approaches a closed one.*

Suppose that after  $\lambda$  cycles of the amplitude  $\mathfrak{A}$  about the neutral state, another smaller cycle of the amplitude  $\mathfrak{a}$ , whose centre is situated at  $j$ , is completed  $\lambda$  times, and then it is just in the stage  $p$ . Then, the yielding at this instant is, by the general equation (6), writing  $\mathfrak{D}$  for  $4\lambda\mathfrak{A} + 4(\lambda + 1)\mathfrak{a} + 1$ ,

(22).

$$\gamma = k \log \frac{I\{\mathfrak{D}-p\}[I\{\mathfrak{D}-p-3\mathfrak{A}\}]^2 \cdots [I\{(4\lambda+1)\mathfrak{a}+j-p+1\}]^2 \cdots [I\{\mathfrak{a}+j-p+1\}]^2}{[I\{\mathfrak{D}-p-\mathfrak{A}\}]^2 [I\{\mathfrak{D}-p-5\mathfrak{A}\}]^2 \cdots [I\{(4\lambda+3)\mathfrak{a}+j-p+1\}]^2 \cdots [I\{3\mathfrak{a}+j-p+1\}]^2}$$

Hence the difference between the amounts of yielding at two consecutive stages is

$$\frac{\Delta \gamma}{\Delta p} = k \log \frac{\{\mathfrak{D}-p\}[\{\mathfrak{D}-p-3\mathfrak{A}\}]^2 \cdots [4(\lambda+1)\mathfrak{a}+j-p+1]^2 \cdots [\mathfrak{a}+j-p+1]^2}{[\mathfrak{D}-p-\mathfrak{A}]^2 [\mathfrak{D}-p-5\mathfrak{A}]^2 \cdots [3\mathfrak{a}+j-p+1]^2} \quad (23).$$

Putting herein  $p=j$ , we have the increase of yielding at the stage corresponding to the centre of the smaller cycle in its increasing stage. The result is

$$\left\{ \frac{\Delta \gamma}{\Delta p} \right\}_{p=j} = k \log \frac{\{\mathfrak{D}-j\}[\{\mathfrak{D}-j-3\mathfrak{A}\}]^2 \cdots [4(\lambda+1)\mathfrak{a}+1]^2 \cdots [\mathfrak{a}+1]^2}{[\mathfrak{D}-j-\mathfrak{A}]^2 [\mathfrak{D}-j-5\mathfrak{A}]^2 \cdots [3\mathfrak{a}+1]^2} \begin{matrix} \leq 0 \\ \geq 0 \end{matrix} \quad (24).$$

whose sign wholly depends on the relative values of  $\mathfrak{A}$ ,  $\mathfrak{a}$  and  $j$ . This is a more general case of the fourth proposition.

Taking its differential with respect to  $j$ , we have

(25).

$$\frac{\Delta}{\Delta j} \left\{ \frac{\Delta \gamma}{\Delta p} \right\}_{p=j} = k \log \frac{\{\mathfrak{D}-j-1\}[\{\mathfrak{D}-j-\mathfrak{A}\}][\{\mathfrak{D}-j-1-3\mathfrak{A}\}]^2 \cdots [\mathfrak{A}+4(\lambda+1)\mathfrak{a}-j-1]^2}{\{\mathfrak{D}-j\}[\{\mathfrak{D}-j-1-\mathfrak{A}\}]^2 [\{\mathfrak{D}-j-3\mathfrak{A}\}]^2 \cdots [\mathfrak{A}+4(\lambda+1)\mathfrak{a}-j]^2} < 0$$

which is always negative since we have

$$\frac{\mathfrak{D}-j-1}{\mathfrak{D}-j} < 1; \frac{\{\mathfrak{D}-j-\mathfrak{A}\}[\{\mathfrak{D}-j-1-3\mathfrak{A}\}]}{\{\mathfrak{D}-j-1-\mathfrak{A}\}[\{\mathfrak{D}-j-3\mathfrak{A}\}]} = \frac{H}{H+2\mathfrak{A}} < 1; \text{ etc. etc.}$$

PROPOSITION VII. *The hysteresis curve, whose amplitude is given, tends to become more and more horizontal when its centre becomes more and more remote from the neutral state of the specimen.*

In the equation (8) put  $\lambda=0$  and  $p=0$ , then the value of  $\gamma$ , which corresponds to the residual after the first cycle, is

$$\gamma_1 = k \log \frac{I(4\mathfrak{A}+1)[I(\mathfrak{A}+1)]^2}{[I(3\mathfrak{A}+1)]^2}$$

while, putting  $\lambda=1$  and  $p=0$ , the residual after the second cycle is

$$\eta_2 = k \log \frac{\Gamma(8\mathfrak{N}+1)[\Gamma(5\mathfrak{N}+1)]^2[\Gamma(\mathfrak{N}+1)]^2}{[\Gamma(7\mathfrak{N}+1)]^2[\Gamma(3\mathfrak{N}+1)]^2},$$

so that the difference of the two is

$$\eta'_2 = k \log \frac{\Gamma(8\mathfrak{N}+1)[\Gamma(5\mathfrak{N}+1)]^2}{[\Gamma(7\mathfrak{N}+1)]^2[\Gamma(4\mathfrak{N}+1)]}.$$

Now, the value given by  $\eta_1$  is what is called *set* by engineers and the value of  $\eta'_2$  is its increase caused by the second cycle. Comparing the absolute values of these two, we easily see that the latter is very small. In a particular case, indeed, where  $\mathfrak{N}=10$ , the value of  $\eta_1$  is  $\{3.825 \log 10\}$  while that of  $\eta'_2$  is only  $\{0.238 \log 10\}$ , which falls almost within the limits of error of observation, or which may be neglected without any serious error. Thus we have

PROPOSITION VIII. *Suppose that we give a set to a specimen by twisting it through a definite angle. A second twisting through the same angle causes little or no further set.*

Lastly, referring to the equations (6) and (7) we see that, since  $\eta$  is a function of several variables, it may have any value whatever, within certain limits, when the amount of couple actually acting upon the specimen i.e.  $p$  or  $n$  is given. Also, from (17) we see that, when  $p$  or  $n$  and  $\eta$  are given,  $\frac{\Delta\eta}{\Delta p}$  or  $\frac{\Delta\eta}{\Delta n}$  may have several different values.

Thus we have :

PROPOSITION IX. *Not only may the specimen be brought to any twisted state, within wide limits, by a given definite couple, but it may have more than one gradient in passing through that state.*

As a particular case of the above, if both  $p$  or  $n$  and  $\eta$  are zero, the specimen is actually free from any external couple and also it is free from any residual. In every respect, there is no external difference between such a piece and a virgin one. Tested with couple, however, it retains latent traces of the twist from which it was lately

released, and it is much more easily twisted in one direction than in the other. This is shown by the fact that  $\frac{\Delta \gamma}{\Delta p}$  and  $\frac{\Delta \gamma}{\Delta n}$  have different values at this stage. Moreover, in this case, though both  $p$  or  $n$  and  $\gamma$  are zero,  $-\frac{\Delta \gamma}{\Delta t}$  is not generally zero; so that we have

PROPOSITION X. *A lately twisted specimen, which is actually in the non-twisted state, becomes gradually twisted with the lapse of time without any application of external couple.*

After all, a specimen which has been, twisted at least once can not be really neutral one like a virgin piece. The neutral state is the state of *no internal stress* which is the same as that which Saint-Venant used as a means of deducing the uniqueness of the solution of the elastic equations under the name “L'état dit naturel ou primitif.” An interesting explanation for the internal state of molecular equilibrium by Sir W. Thomson<sup>(1)</sup> may be cited here; “.....the outer particles will be strained in the direction opposite to that in which it was twisted, and the inner ones in the same direction as that of the twisting, the two sets of opposite couples thus produced among the particles of the bar balancing one another.”

The further nature of the Hysteresis function is to be most clearly comprehended by tracing the curve representing it. The result of a laborious calculation is graphically shown in the figure in Pl. XIV. It represents the Hysteresis function for a particular case;  $\mathfrak{A}=10$ ;  $\lambda=0, 1, 2$ ; and  $-10 \leq (p \text{ or } n) \leq +10$ , as well as for two other cases where the amplitude for the one and the centre for the other was changed for different cycles.

As to the Hysteresis curve, it may be necessary to remark that,

(1) Sir W. Thomson. Mathematical and Physical papers. Vol. III.

since the twist consists of two terms, the form of any actual stress-strain curve must be greatly affected in its features by the relative value of the two terms. When the first term, which fulfils Hooke's law, is negligible relatively to the yielding, the curve takes the form given in Pl. XIV. On the other hand, if the yielding is negligible as compared with the principal term, then, as a matter of course, the curve shrinks into a straight line. For any other relative values, the curve takes an intermediate form. Figures in Pl. XV., which have been drawn from the results of actual calculation, show several intermediate forms. The inclined straight line in each figure represents the curve to which it shrinks if the yielding be disregarded. In the following pages, all these mathematical deductions will be experimentally proved.

### VERIFICATION BY EXPERIMENTS.

On gradually releasing a twisted piece of rock from the couple, the specimen shows a tendency to persist in its twisted state, so that there remains some residual twist when all the couple is withdrawn. Moreover, if after withdrawing the whole couple, we begin to reapply it, we find that the specimen is more rigid in one direction than in the other. These facts are graphically shown in Pl. XVI. for the case of sandstone.

When a piece of rock is twisted cyclically within any definite limits of couple, its stress-strain curve approaches a closed one of simple and regular form. The on-curve, however, differs entirely from the off-curve, though they are so related to each other that one, when it is turned through two right angles, nearly coincides with the other. These facts will be better understood from the curves traced in Figs 35-46, Pls. XVII. and XVIII.



The figure in Pl. XVI. gives further illustrations of the effects of torsional hysteresis in causing a loop to be formed on the curves of twist when the couple experiences several cyclic changes with different amplitudes and centres. Here it is to be seen that the greater the amplitude of the cycle, the more the loop tends to become vertical.

Starting from a strained state, a specimen was twisted cyclically, the centre of each cycle being different from that of the others. The result is shown in Pl. XIX., all of the loops produced by the several cycles being nearly similar to one another, though they are widely different in their dimensions. We see, however, that when the amplitude of the cycle is given with regard to the amount of the applied couple, the loop whose centre is further from zero-stress is more horizontal than the other.

Other particulars with respect to the natures of the torsional hysteresis will be learned from the several figures in the annexed plates which have been carefully drawn from experimental results. Comparing the figures in Pls. XVII. and XVIII. with those in Pl. XV., we can not but be struck with the very close coincidence between theory and experiment. Here it is necessary to remark that, though a piece which has been twisted at least once can not be really neutral, yet the process of demagnetization in the case of magnetic hysteresis suggests a means by which any twisted piece can again be brought to a practically neutral state. One example of this process is shown in Fig. 48, Pl. XX. To begin with, in any of the above experiments, this process was applied to get rid of the latent traces of previous history which the specimen may have acquired.

To give a general idea of the comparative magnitudes of the rigidity of several rocks, some of the stress-strain curves for different rocks are drawn, Fig. 49, Pl. XXI., on one and the same scale as

that for soft iron. Corrections due to some differences between their respective dimensions are not taken into account. The horizontal line corresponds to a rigid substance, while the vertical, to an ideal fluid. Numerical values of the modulus of rigidity for different rocks are also added in the annexed table. They serve, however, only to indicate their order of magnitude.

TABLE III.

No.	Rock	Locality	Kind	Mod. of Rigidity	Density	Velocity of Trans. W.
ARCHÆAN ROCKS.				$\times 10^{10}$		Kilom.÷Sec.
18	Chlorite-schist	Chichibu	Metamorphic	20.0—24.1	2.82	2.70—2.89
8	Serpentine	Chichibu	Eruptive	24.8—52.2	2.71	3.03—4.40
31	Quartz-schist	Gumma	(Altered) Metamorphic	24.5—28.9	2.64	3.06—3.29
42	Mica-schist	Ibaraki	Metamorphic	1.77	2.64	0.82
7	Peridotite (Serpentinized)	Kuji	Eruptive (Altered)	22.3	2.61	2.93
PALÆOZOIC ROCKS.						
32	Pyroxenite	Gumma	Sedimentary (Metamorphized)	23.0—49.0	2.90	2.82—4.33
12	Clay-slate	Shiga	Sedimentary	2.93	2.74	1.03
21	Limestone	Chichibu	Sedimentary ?	7.73	2.64	1.71
6	Marble	Kuji	Sedimentary (Metamorphized)	8.63—9.15	2.64	1.82—1.85
13	Clay-slate	Shiga	Sedimentary	10.82	2.58	2.05
10	Granite	Kagawa	Eruptive	5.71	2.57	1.49
9	Granite	Mikage	Eruptive	16.9	2.54	2.58
14	Red Schalstein	Shiga	Sedimentary	7.79	2.43	1.79
TERTIARY ROCKS.						
5	Rhyolite	Yechizen	Eruptive	2.74—3.12	2.36	1.07—1.16
4	Sandstone	Ki-i	Sedimentary	0.72—1.25	2.21	0.57—0.94
3	Sandstone	Chiba	Sedimentary	0.41—2.64	2.20	0.43—1.09
2	Tuff	Izu	Sedimentary	5.73—6.18	1.91	1.74—1.80
DILUVIUM ROCKS.						
17	Andesite	Gumma	Eruptive	8.09	2.63	1.75
1	Andesite	Sagami	Eruptive	8.62	2.59	1.76
16	Andesite (Porous)	Gumma	Eruptive	2.17	2.32	0.97

## THE EFFECT OF TEMPERATURE.

The present arrangement being unsuitable for heating and cooling the specimen, my intention was rather to ascertain only the order of the experimental error due to the temperature-variation in the laboratory. To get rid of the effect of the yielding, the specimen to be tested was subjected to a constant couple during three days and nights. Then, the creeping due to the yielding having become comparatively small, the temperature-variation of the twist was observed. The time-variations of both the temperature and the twist were, as they are shown in Figs. 50–52 in Pl. XXII., similar to each other. In Fig. 53 in the same plate, we see the increase of twist plotted against the corresponding rise of temperature. The curve, as a whole, expresses the *simple proportionality between the two elements*. We find, however, one remarkable fact that the temperature-variation of the twist has a *minimum value* in the neighbourhood of  $9^{\circ}\text{C}$ . It may be questionable whether this is a general property of all rocks or merely special to that specimen alone. By the way, it may be cited here that, from the experiment of G. Wertheim<sup>(1)</sup>, the stretch modulus of iron and steel seems to have a maximum value at or a little below  $100^{\circ}\text{C}$ ., since at  $200^{\circ}$  it is sensibly the same as at  $-15^{\circ}$ .

Lastly, we must not neglect to remark here that though the temperature-variation of the twist is unexpectedly great, yet it is almost negligible as compared with the total amount of the twist and also with that of the yielding. Indeed, the increase of twist per degree of temperature-rise is less than  $3 \times 10^{-3}$  of its total amount in sandstone.

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(1) G. Wertheim. Annales de chimie. T. XV. 1815.

## APPENDIX.

RELATION BETWEEN THE VELOCITY OF PROPAGATION AND  
THE AMPLITUDE OF SEISMIC WAVES.

It is a well known fact that, in any earthquake, the principal shocks are always preceded by tremors of small amplitude. On the supposition that the waves of the tremors and of the principal shocks are all generated simultaneously at one and the same origin, the above facts show that the velocities of the tremors are much greater than that of the principal shocks. Indeed, according to Professor Omori<sup>(1)</sup>, the velocities of the first and second tremors are equal to 12·8 and 7·2 kilometres per second, while that of the principal shocks is only about 3·3 kilometres per second. An explanation of this fact is given by Professor H. Nagaoka in his essay above cited, from the consideration that there exists a stratum of maximum velocity of propagation in the earth's crust. The causes of this simple fact must possibly be of a very complicated nature. In so far, however, as the wave-velocity is a function of the elastic constants, the elastic yielding can never be disregarded in the determination of the velocities of seismic waves. In the case of sound waves, the *Newtonian Velocity* deduced from Boyle's law is much smaller than that found by observation. Taking, however, the heating by condensation and cooling by rarefaction into account, Laplace obtained a result agreeing with experiment. So, in the case of seismic waves, the greater part, at least, of the discrepancy must be due to the assumption of Hooke's law. Even in the weakest earthquake, the strain associated with the principal shocks must be, I think, far beyond the limits of elasticity.

If what I have stated above be the case, the effect of the yielding

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(1) F. Omori. Publ. of the E. I. Committee in Foreign Languages. No. 5. 1901.

would be, at least, *one of the principal causes of the diminution of velocity*. In the equation (17) put  $p=0$  and  $\lambda=1$ , then

$$\left\{ \begin{array}{l} \Delta \gamma \\ \Delta p \end{array} \right\}_{p=0, \lambda=1} = k \log \frac{\{8\mathfrak{A}+1\}\{5\mathfrak{A}+1\}[\mathfrak{A}+1]^2}{[7\mathfrak{A}+1][3\mathfrak{A}+1]^2} = \tau_2 \quad \text{say.}$$

This value of  $\frac{\Delta \gamma}{\Delta p}$ , expressed as a function of the amplitude  $\mathfrak{A}$ , represents the amount of the increase of twist due to the yielding, per unit increase of couple in the stage of zero couple after one cycle of twisting through an amplitude  $\mathfrak{A}$ . Now, the actual amount of twist is the sum of two terms ; i.e.

$$\tau = \tau_1 + \tau_2$$

where  $\tau_1$  is the term which fulfils Hooke's law. Let  $v$  and  $c$  be the velocity and factor of proportionality respectively, then we have

$$v = c\{\tau_1 + \tau_2\}^{-\frac{1}{2}} = v_0 \left\{ 1 + \frac{\tau_2}{\tau_1} \right\}^{-\frac{1}{2}}$$

If the yielding be disregarded, then neglecting  $\frac{\tau_2}{\tau_1}$  we have

$$v = v_0$$

so that *all waves with different amplitudes propagate with a common velocity if, and only if, the stratum of rocks through which they propagate does not yield*.

*When the yielding is enormous, which is the case for a loose stratum such as the earth's crust, the velocity decreases very rapidly when the amplitude of the wave increases.* The quantitative relation between these two elements is given in the following table.

TABLE IV.

$\mathfrak{A}$ Particular unit	1	2	3	4	5	6	7	8	9	10
$\frac{r}{r_0}$ (Ideal)	1.00	0.98	0.95	0.90	0.86	0.84	0.82	0.80	0.39	0.38
$\frac{r}{r_0}$ (Marble)	1.00	0.96	0.94	0.92	0.91	0.90	0.89	0.88	0.87	0.86

The values of  $\frac{v}{v_0}$  given in the second row correspond to the case where one may be neglected as compared with  $\frac{\tau_2}{\tau_1}$ ; while those in the last row correspond to the case where the waves propagate through an infinitely extended uniform stratum of marble. The last is calculated using a value of  $k$  determined experimentally, the result being traced in Fig. 38, Pl. XVIII.

Quite independently of the above hysteresis function, the ratio of velocities of several waves through a stratum of serpentine and pyroxenite are obtained from the experiments shown in Pls. IV<sub>a</sub> and IV<sub>b</sub>.

TABLE V.

Ratio of Amplitudes.		1	30	75	115	185
Ratio of Velocities.	Serpentine	1.30	0.78	0.73	0.71	0.71
	Pyroxenite.	1.00	0.76	0.71	0.70	0.69

Here we can not omit to remark that, though the values given in TABLE IV. may be absurd as it stands on the foundation of the hysteresis function, those in TABLE V. can not be disputed by any one even with the result of the most subtle analysis, provided that the fundamental formula, which expresses that the velocity varies as the square root of the rigidity-modulus of the medium through which the wave propagates, be granted.

By the equation (25), it can not be disregarded that the velocity of propagation increases when the stratum of rock, through which the wave propagates, is in a strained state. Thus, for example, the seismic wave would probably propagate more quickly along a mountain chain than in uniform plain land. This variation, however, is much smaller than the former.

From what has been above discussed, it may safely be said that

of several waves, the one whose amplitude is smaller has necessarily a greater velocity than the other. When the yielding predominates, the velocity may become two or three times smaller as the amplitude becomes some ten times greater. The disturbance of smallest amplitude will first make its appearance as the beginning of the preliminary tremor, followed by waves of greater amplitudes in succession. Other disturbances, propagating through different strata or of other origin, would probably appear intermixed with the former, giving a somewhat irregular record on the seismograph.

In TABLE III., the velocities of propagation of transversal waves through several rocks are also added. They serve only to give a general idea of the order of magnitude, since the velocity is never constant for any specimen, as there exists more or less yielding.

In conclusion, I wish to express my great indebtedness to Mr. Fukuchi for valuable information concerning the geological and petrological character of the specimens examined in the present experiment. My best thanks, however, are due to Professor H. Nagaoka and also to Professor A. Tanakadate, without whose valuable advice and most kind guidance I could scarcely have succeeded in carrying out this experiment.

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### EXPLANATION OF PLATES.

Remarks. Unit of couple =  $6.712 \times 10^6$  c.g.s. unit; unit of twist =  $1.845 \times 10^{-3}$  radian; unit of time = one minute.

Pl. I.

**Fig. 1.** Preliminary experiment on Specimen No.  $3_3$  shows great deviation from Hooke's law and the existence of torsional hysteresis.

Pl. II.

**Figs. 2 and 3.** Front and side views respectively of the twisting apparatus.

„ 4. Plan of the whole arrangement.

„ 5. Framework carrying the mirror.

Pl. III.

**Fig. 6.** Curve A. Yielding of the Support. Curve B. Twist of Specimen No.  $12_1$ . This shows that the result of observation is not disturbed by the yielding of the support.

Pl. IV<sub>a</sub>, and IV<sub>b</sub>.

**Figs. 7 and 8.** Effect of cyclical application of positive and negative couples with their several amplitudes. They show the existence of torsional hysteresis, even in the case where Hooke's law is tolerably fulfilled. Specimens, No.  $32_1$  and  $8_2$ .

Pl. V.

**Fig. 9.** Relation between the negative couple required to annihilate the residual twist and the original couple. Deduced from the above observations.

„ 11a. Relation between the modulus of rigidity and the amplitude: Specimens No.  $32_1$  and  $8_2$ .

„ 11b. Relation between the residual twist and the amplitude.

Pl. VI.

**Fig. 10.** Torsional hysteresis in Specimen No.  $3_3$ . Showing the indefiniteness of the modulus of rigidity.

Pl. VII.

**Figs. 12 and 13.** On-curve and Off-curve respectively. Each series of observations admits of being connected by a straight line, so that Hooke's law is fulfilled. The difference of inclinations, however, shows the ambiguity of the modulus of rigidity. Specimen No.  $4_2$ .



Pl. VIII.

**Fig. 14.** Yielding of Specimen No.  $3_2$  under constant couple. The resisting masses are different for the two curves.

„ 23 and 24. Recovery from the yielding. Specimen No.  $4_1$  was subjected to constant couple during a week.

„ 27. Theoretical curve for recovery, deduced from hysteresis function.

Pl. IX.

**Fig. 15.** Yielding of Specimen No.  $4_1$  under constant couples. Constant couple has different values for different curves.

„ 18. Theoretical curves for yielding.

Pl. X.

**Figs. 16 and 17.** Relation between the rate of yielding and the time-element. Specimen No.  $4_1$ . Full lines are theoretical curves. Eight straight lines and hyperbolas should be drawn to correspond to all points.

Pl. XI.

**Figs. 19-22.** Yielding after a long time. Specimen No.  $4_1$ .

Pl. XII.

**Fig. 25.** Effect of the elastic recovery on the cycles. The specimen, No.  $3_3$ , was subjected under a constant couple during 306.5 hours, and then that strained state was taken as the centre of cycle.

Pl. XIII.

**Fig. 26.** Twisting and untwisting—no negative couple applied—of the specimen No.  $3_3$ .

Pl. XIV.

**Fig. 28.** Hysteresis function (due to the elastic yielding).

Pl. XV.

**Figs. 29-33.** Examples of the hysteresis due to the elastic yielding, calculated from the hysteresis function by giving different values to the constant involved in the function. The inclined straight line in each curve shows how the curve shrinks if the yielding be disregarded.

Pl. XVI.

**Fig. 34.** Torsional hysteresis of a piece of sandstone, No.  $3_3$ .

Pls. XVII. and XVIII.

**Figs. 35-46.** Examples of torsional hysteresis in several rocks of different

kinds. Specimens: No.  $3_2$ ;  $3_1$ ;  $5_2$ ;  $6_1$ ;  $6_2$ ;  $10_1$ ;  $9_1$ ;  $8_1$ ;  $7_2$ ;  $31_2$ ;  $18_1$ ;  $17_2$ . These are to be compared with the theoretical curves in Pl. XV.

Pl. XIX.

**Fig. 47.** This shows that the modulus of rigidity increases when the specimen is in a strained state. No.  $3_3$ .

Pl. XX.

**Fig. 48.** Neutralization of a non-virgin piece. No.  $16_1$ .

Pl. XXI.

**Fig. 49.** Gradual diminution of rigidity, from rigid substance to perfect fluid. Axes of abscissa and ordinate correspond to rigid substance and perfect fluid respectively. Specimens: soft iron; No.  $7_1$ ; No.  $17_2$ ; No.  $14_1$ ; No.  $2_1$ ; No.  $16_1$ ; No.  $3_1$ ; No.  $42_1$ .

Pl. XXII.

**Figs. 50-52.** In each figure, the upper curve shows the variation of temperature with time, while the lower that of twist, the couple being constant. Specimen No.  $4_1$ .

**Fig. 53.** Relation between the temperature and the amount of twist.



Fig. 1.  
No. 33.  
Sandstone.

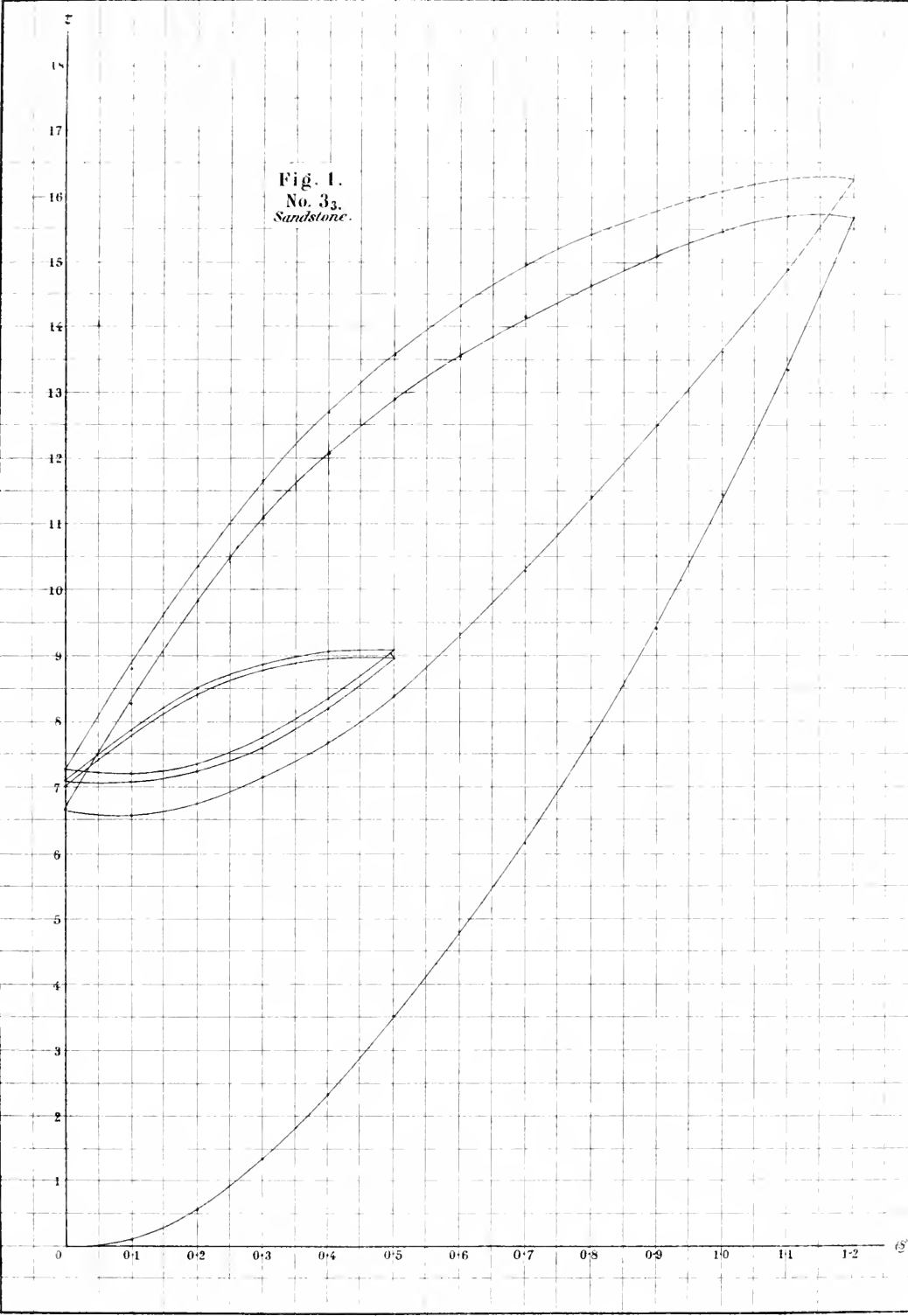




Fig. 2.  
*Front-view*

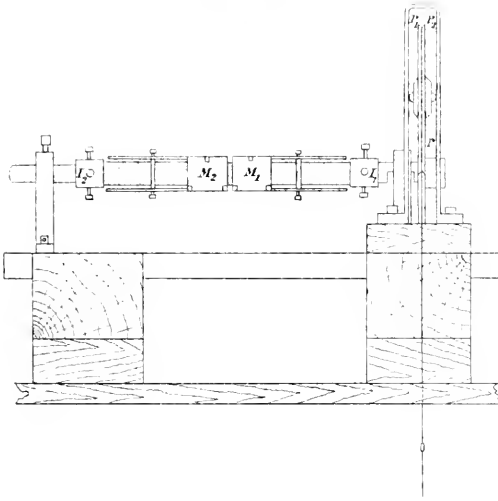


Fig. 3.  
*Side-view*

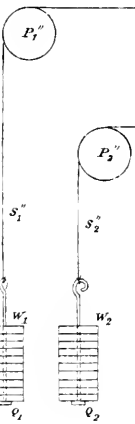
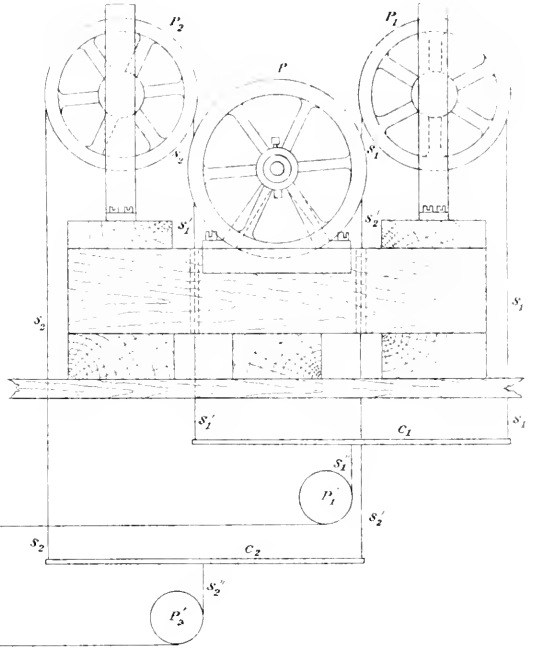


Fig. 5.  
*Frame*

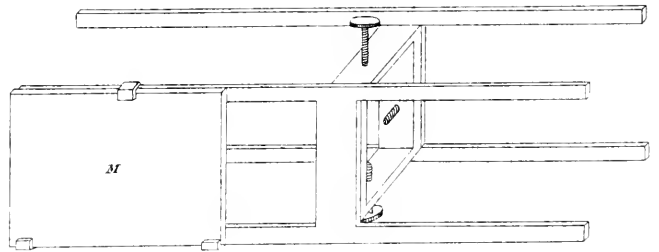


Fig. 4.  
*Plan of the arrangement*





Fig. 6.  
No. 12<sub>1</sub>.  
*Clay Slate.*

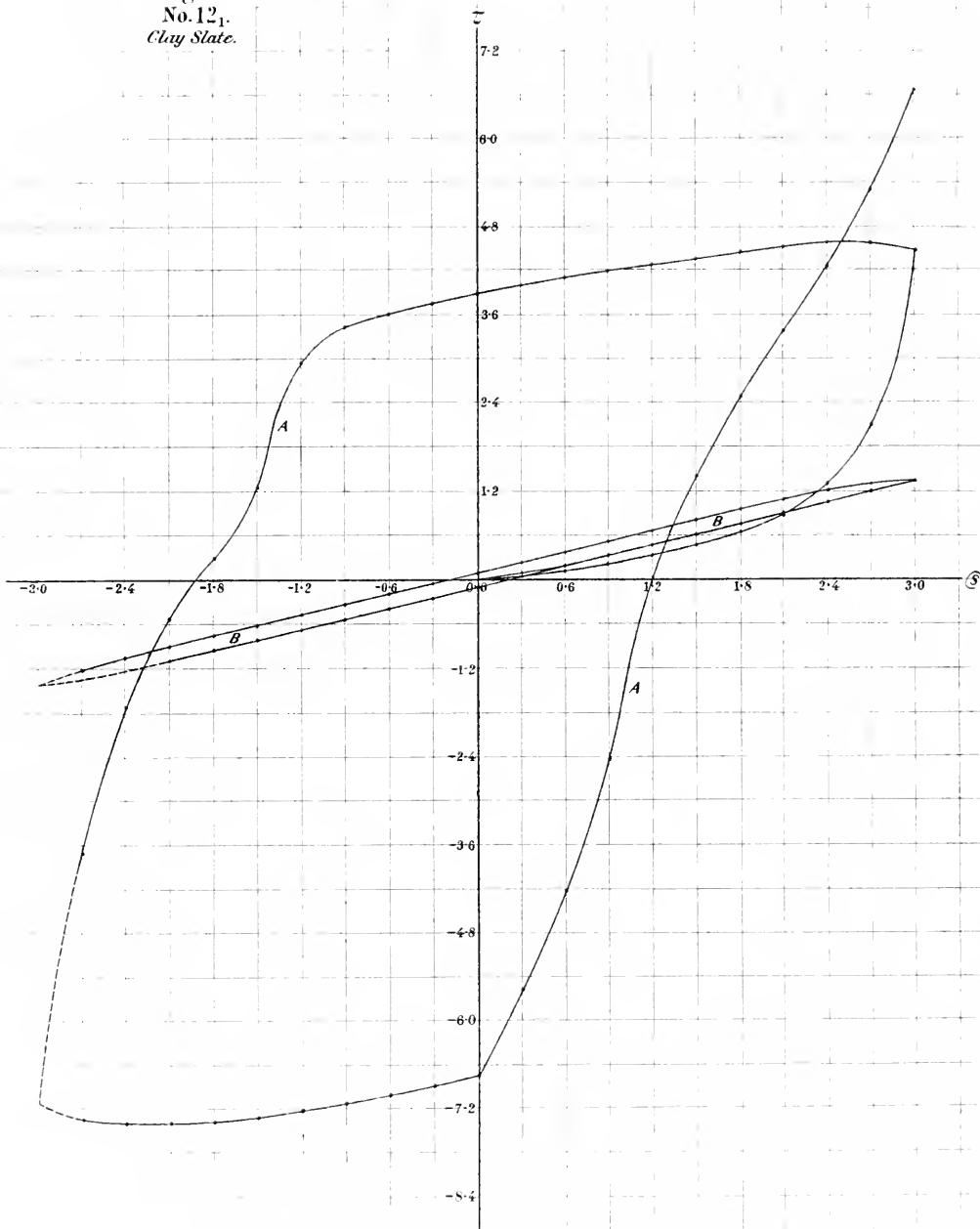
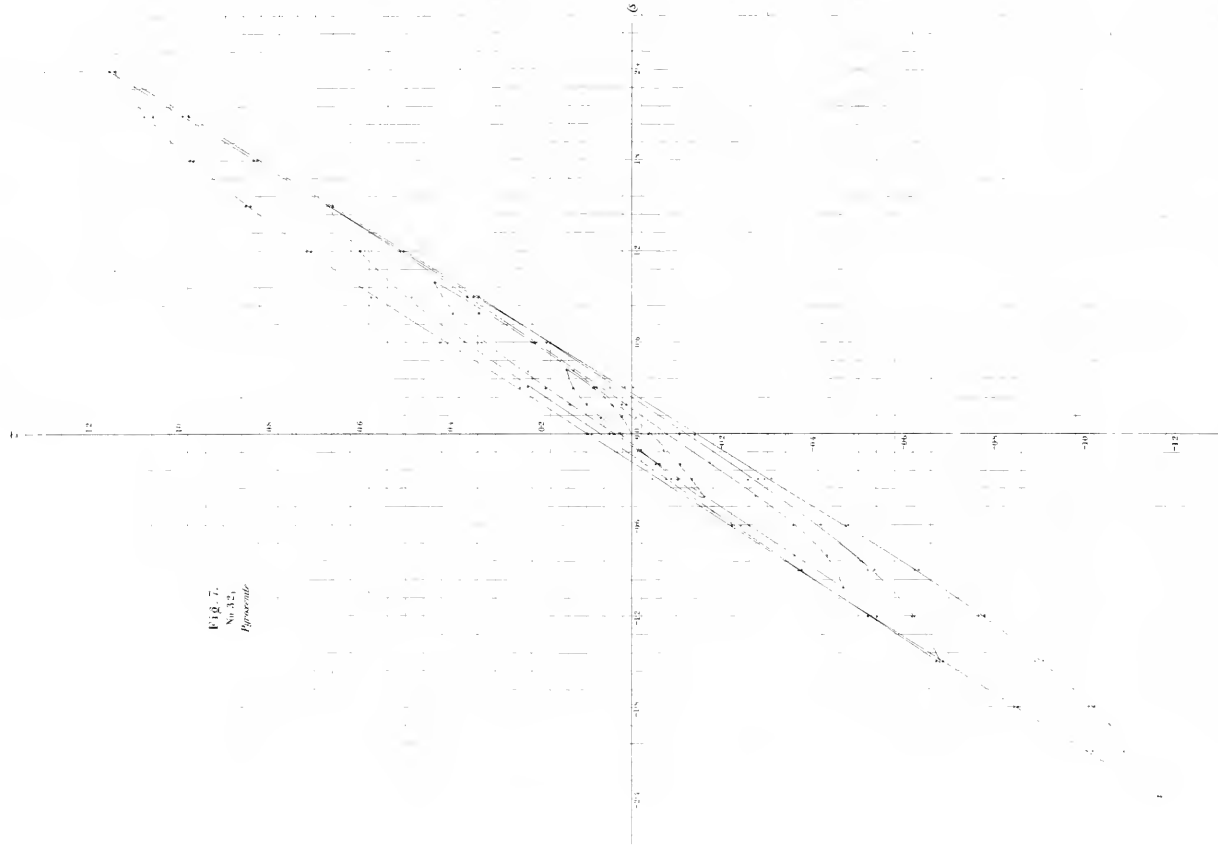






Fig. 7.  
No. 324.  
*Pyrosoma*









Modulus of Rigidity

Fig. 11<sub>a</sub>

Serpentine.  
Pyroxenite.

Fig. 11<sub>b</sub>

Pyroxenite.  
Serpentine.

Fig. 9.

Pyroxenite.  
Serpentine.

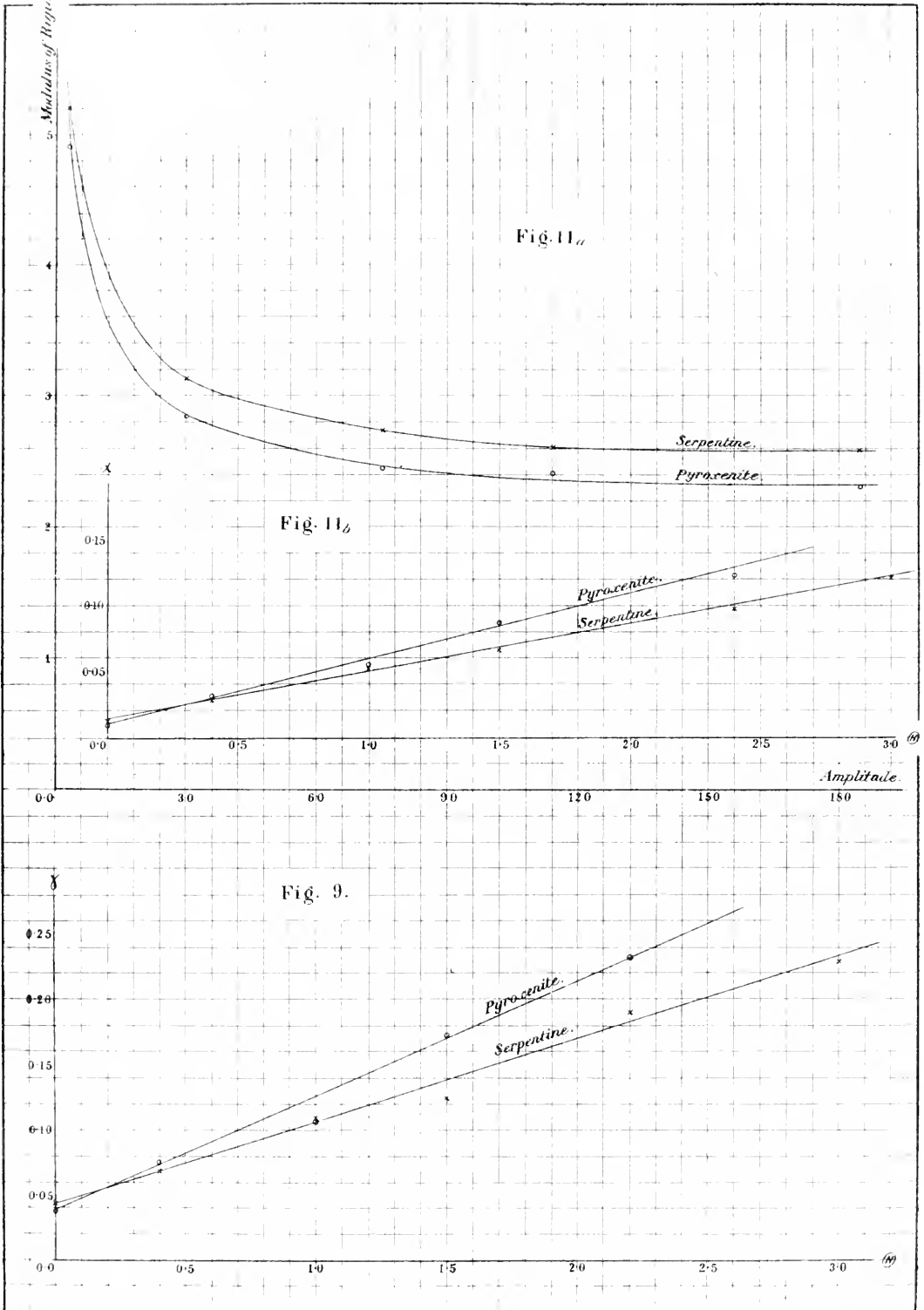
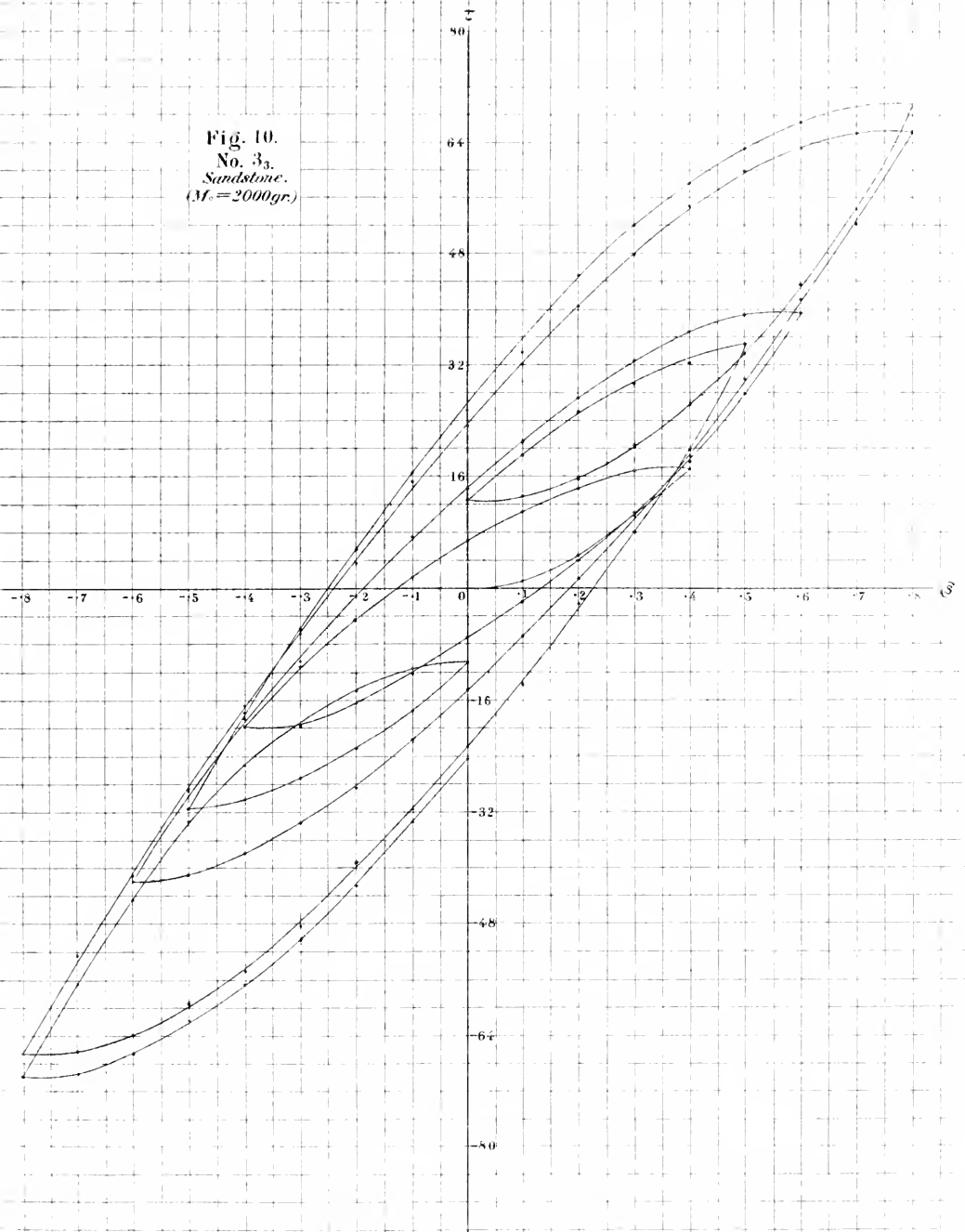




Fig. 10.  
No. 33.  
Sandstone.  
( $M_s = 2000\text{gr.}$ )







No. 42.  
Sandstone.

Fig. 13.  
*Off-curve.*

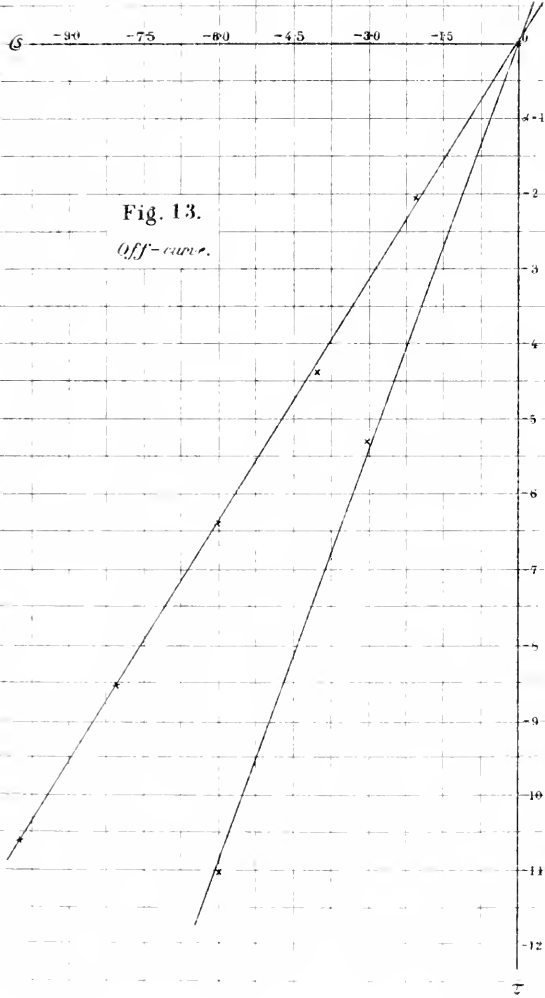


Fig. 12.  
*On-curve.*

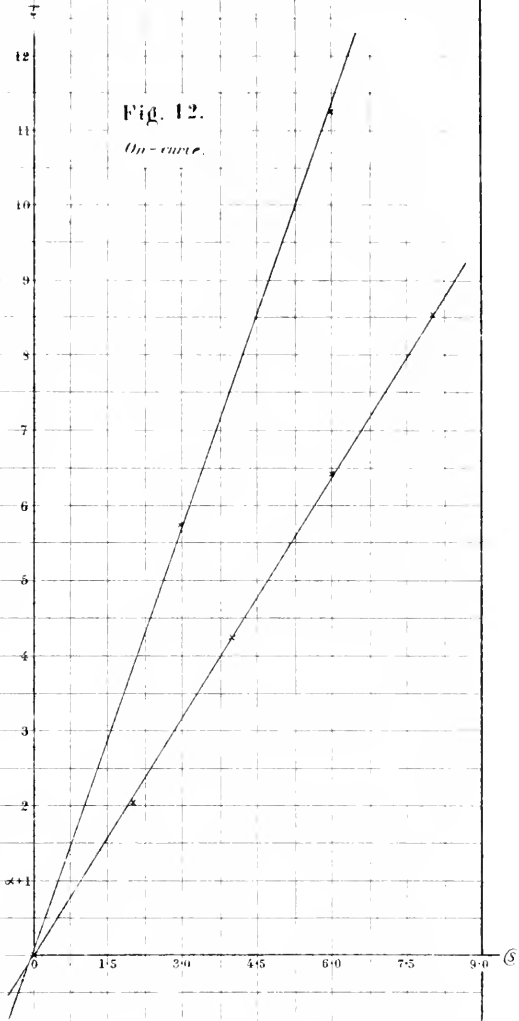




Fig. 14.  
No. 32.  
Sandstone.

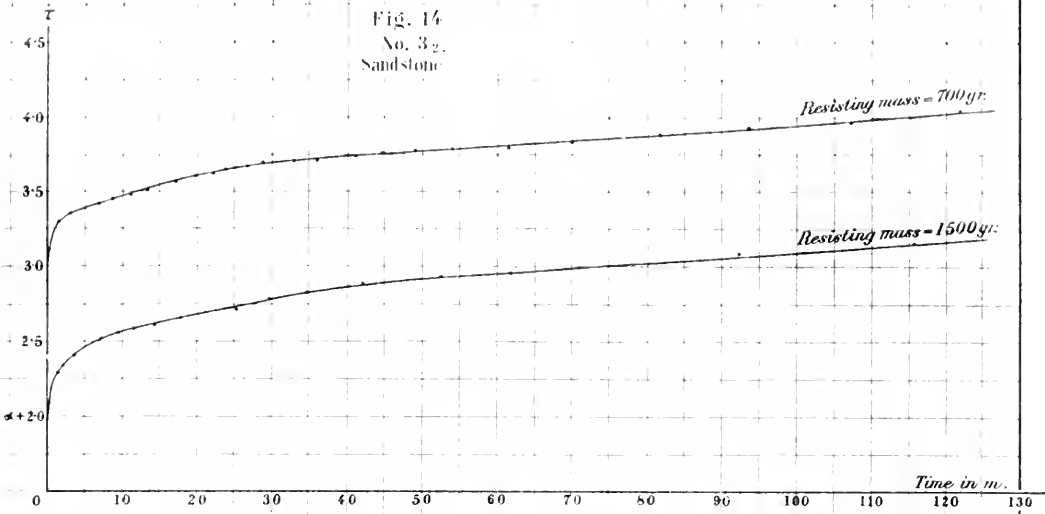


Fig. 23.  
No. 41.  
Sandstone.

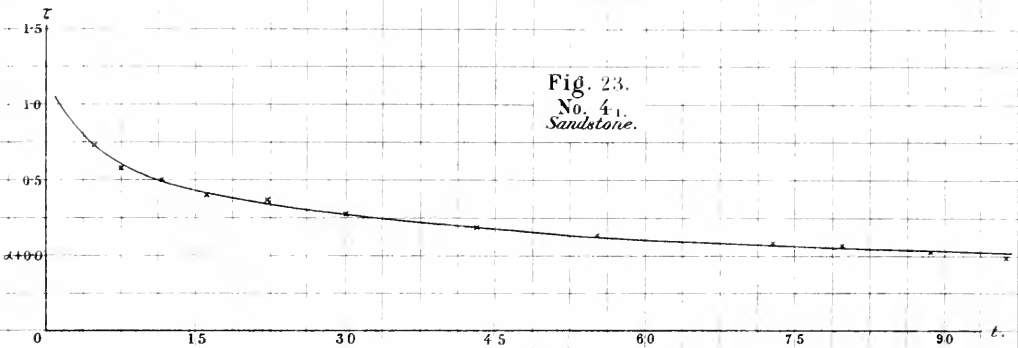


Fig. 24.  
No. 41.  
Sandstone.

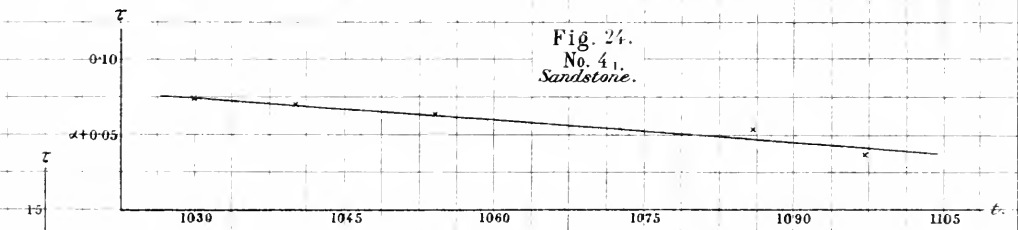
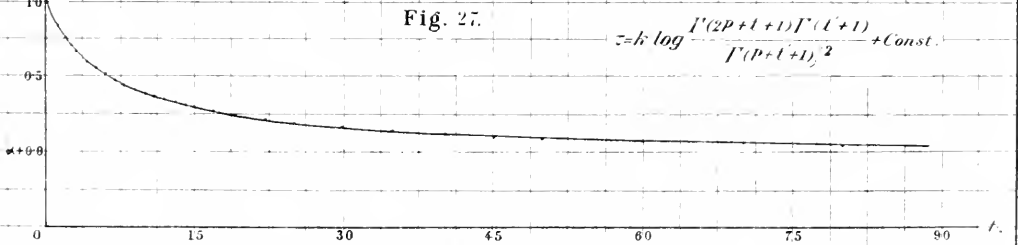


Fig. 27.



$$z = k \log \frac{\Gamma(2p+1+1)\Gamma'(1+1)}{\Gamma'(p+1+1)^2} + \text{Const.}$$



Fig. 18.

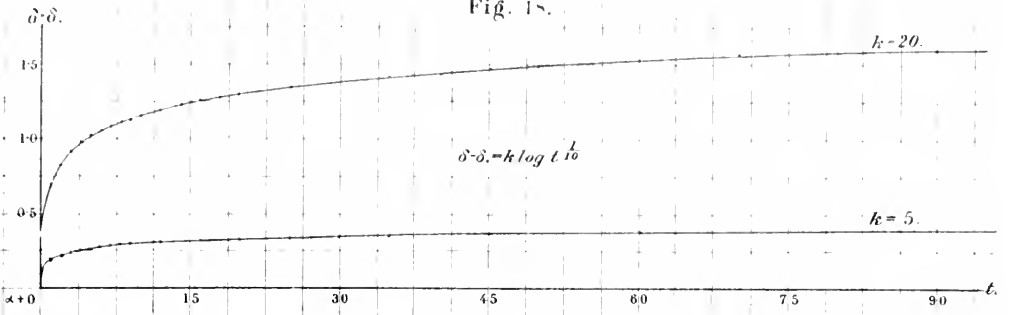
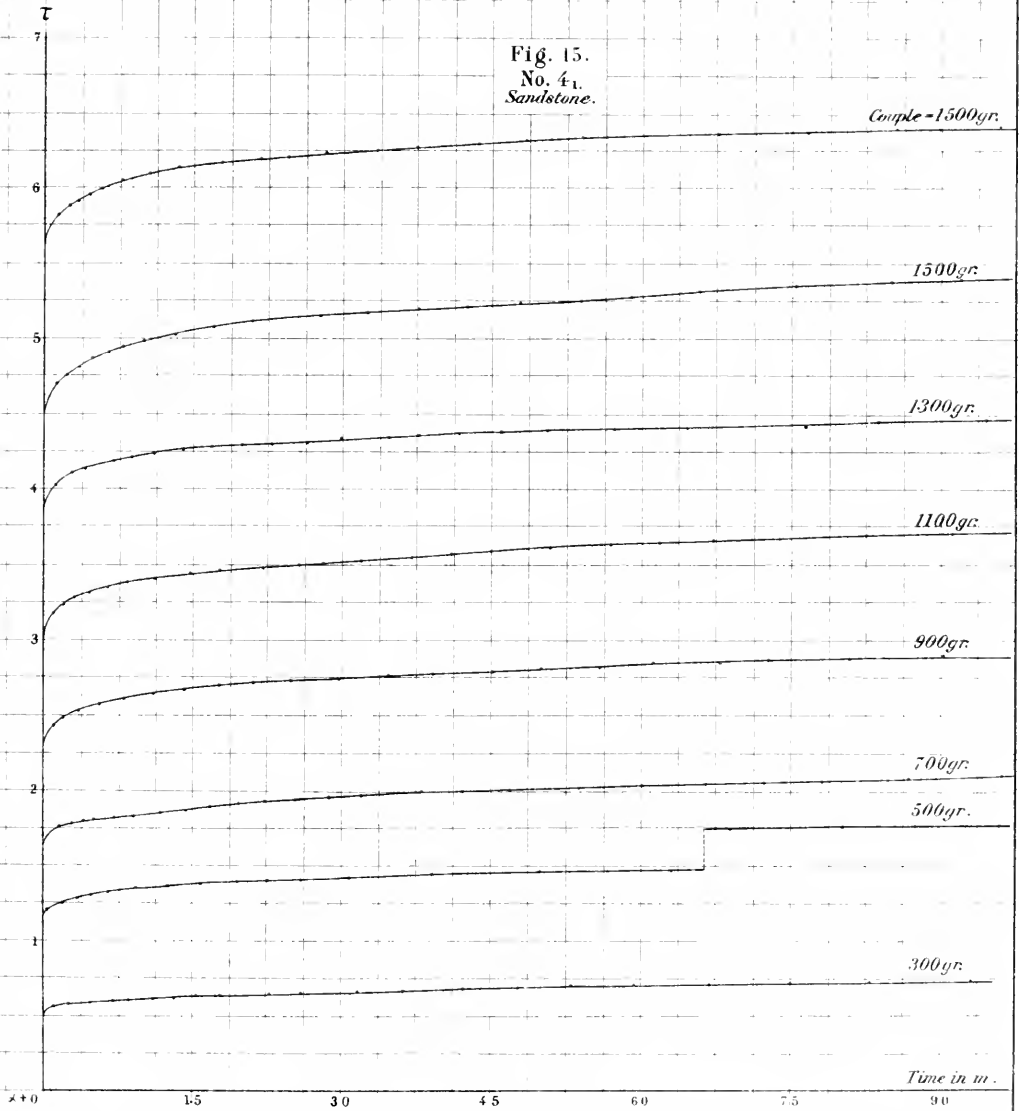


Fig. 15.  
No. 41.  
Sandstone.





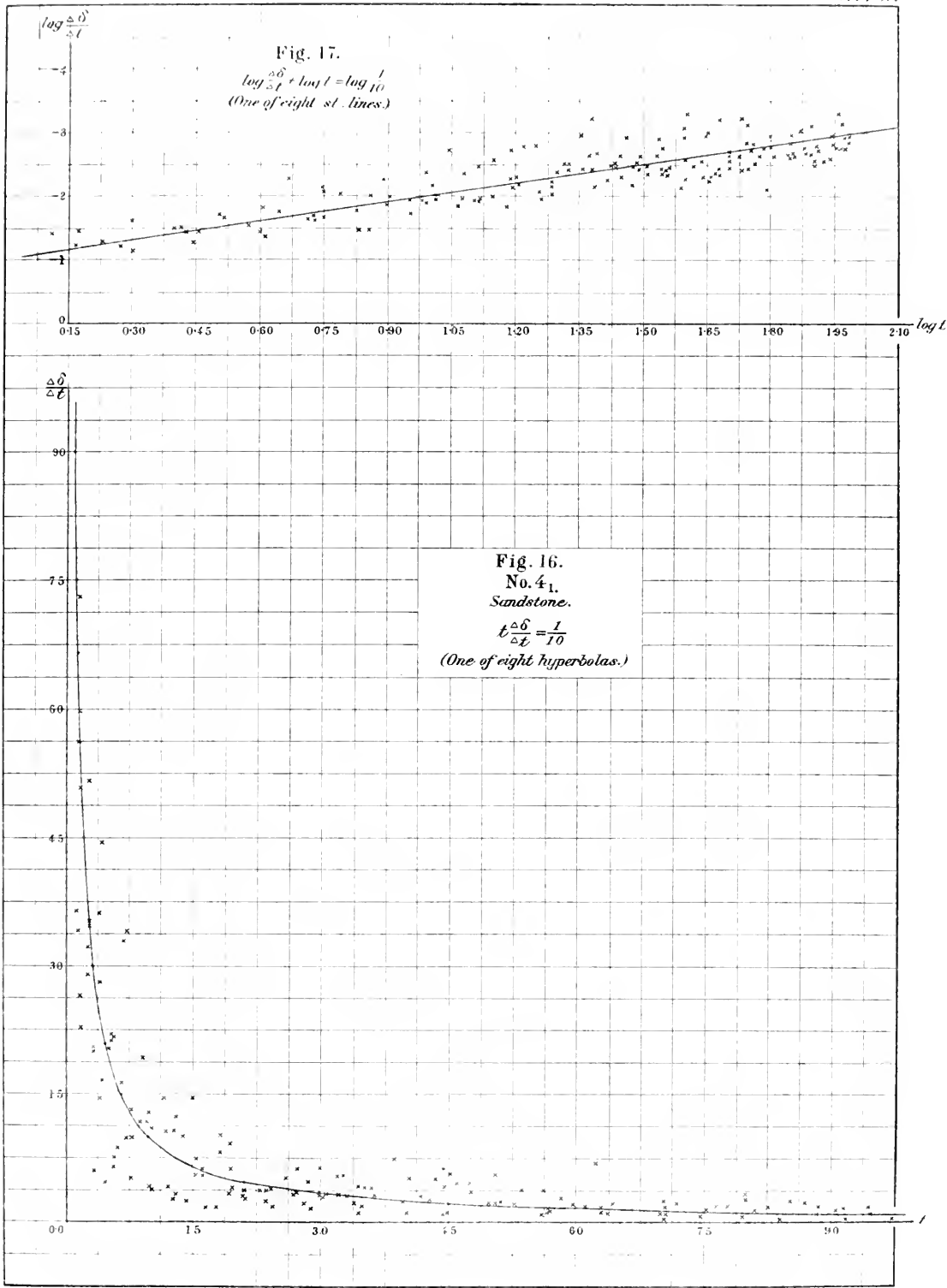






Fig. 19.

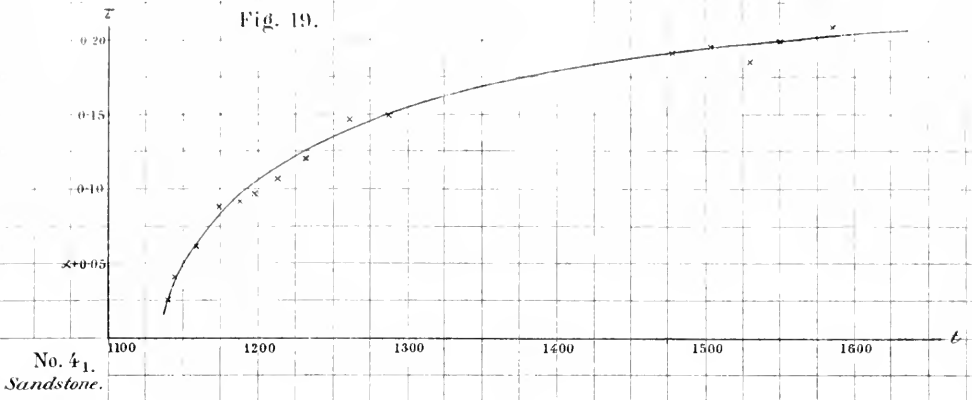


Fig. 20.

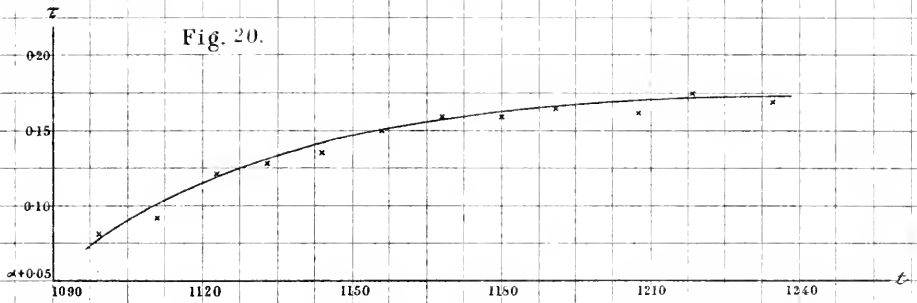


Fig. 21.

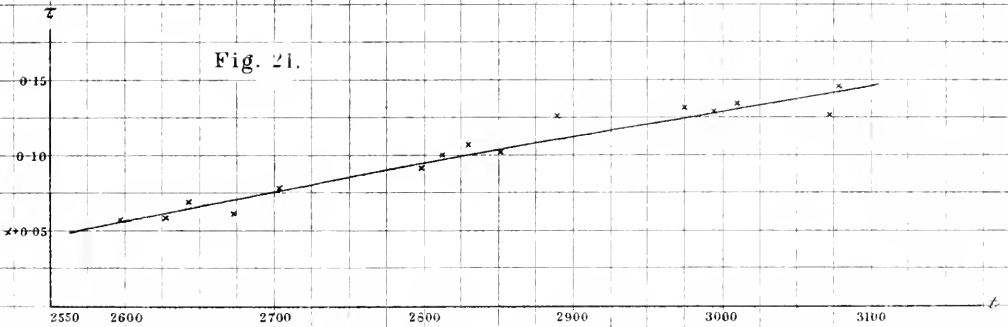


Fig. 22.

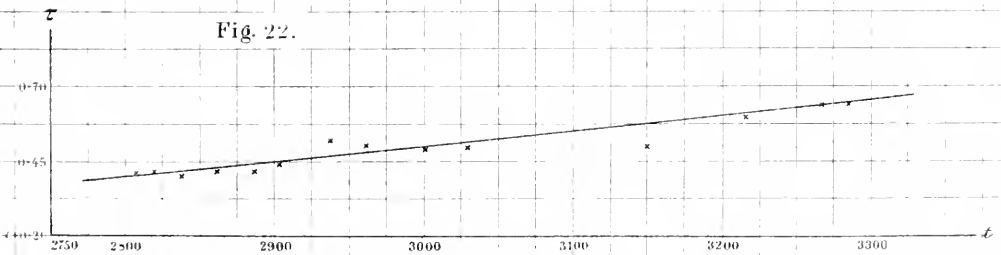




Fig. 25.  
No. 3a.  
*Sandstone*

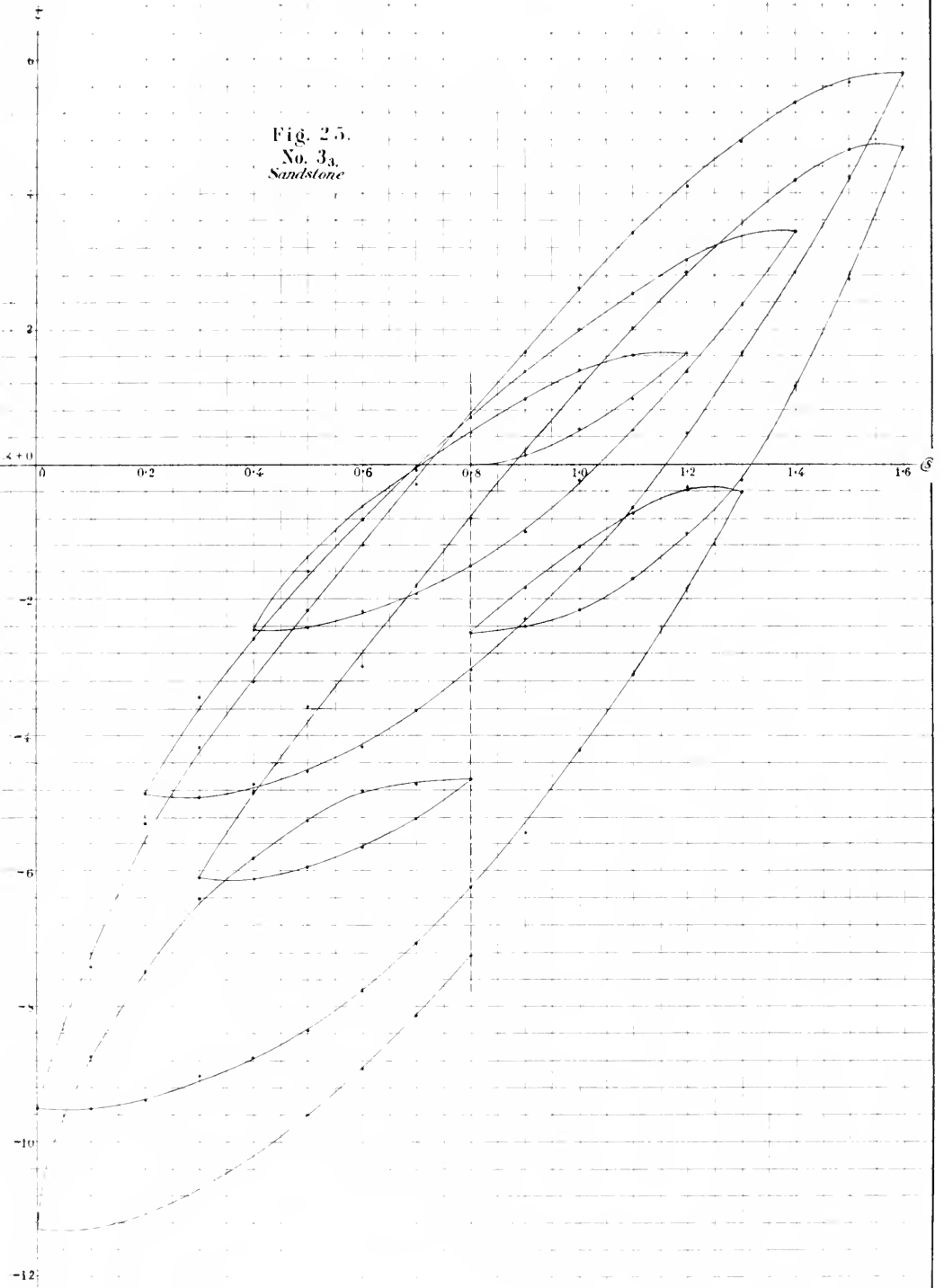




Fig. 26.  
No. 3<sub>a</sub>.  
Sandstone.

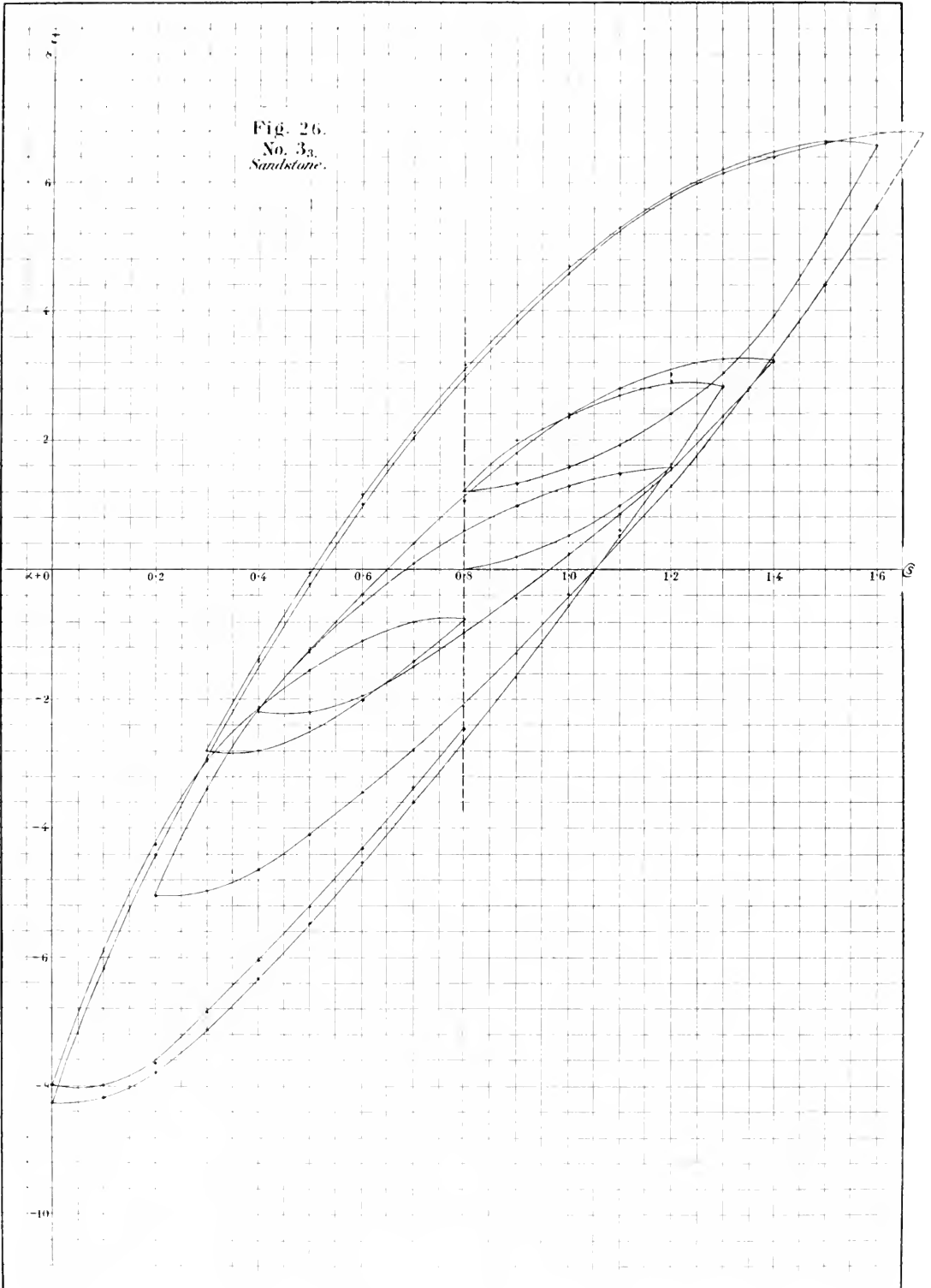




Fig. 25.  
Particular case of  
Formule 6 and 7.

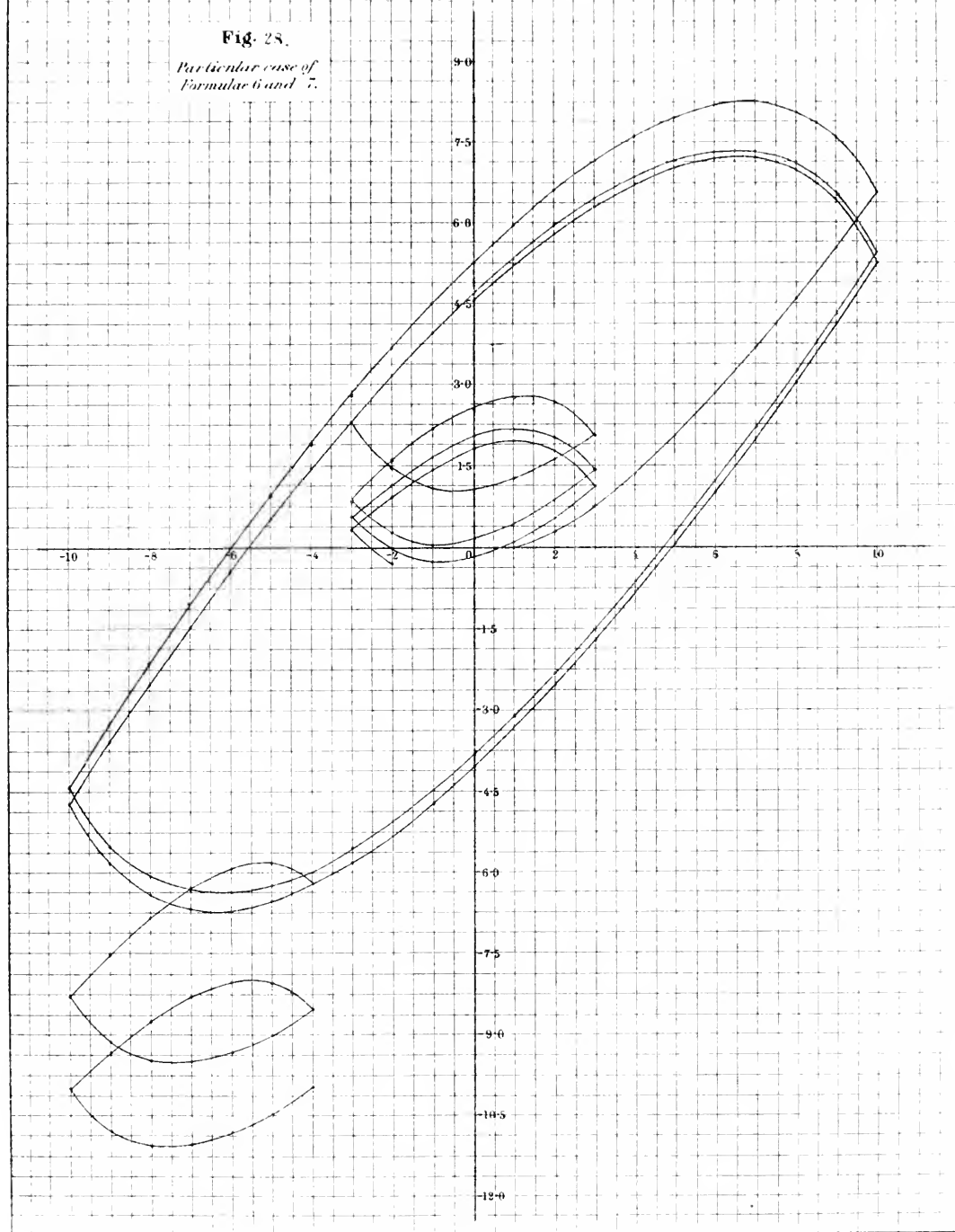






Fig. 29.

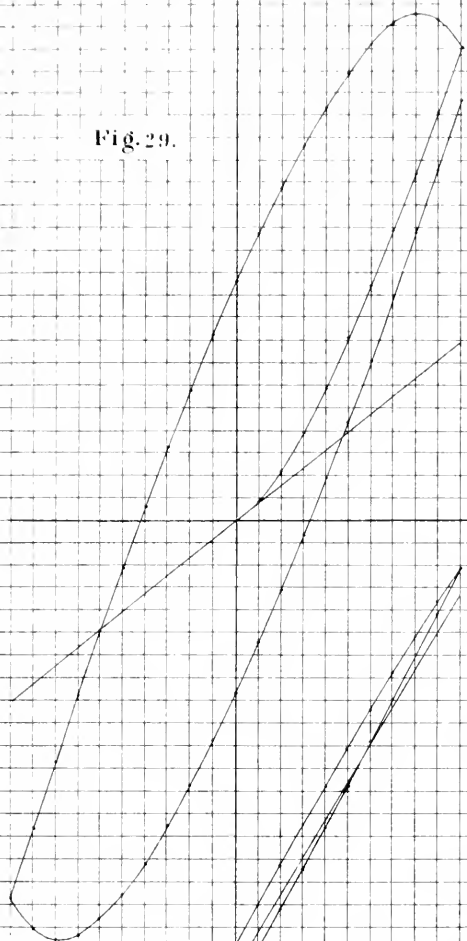


Fig. 31.

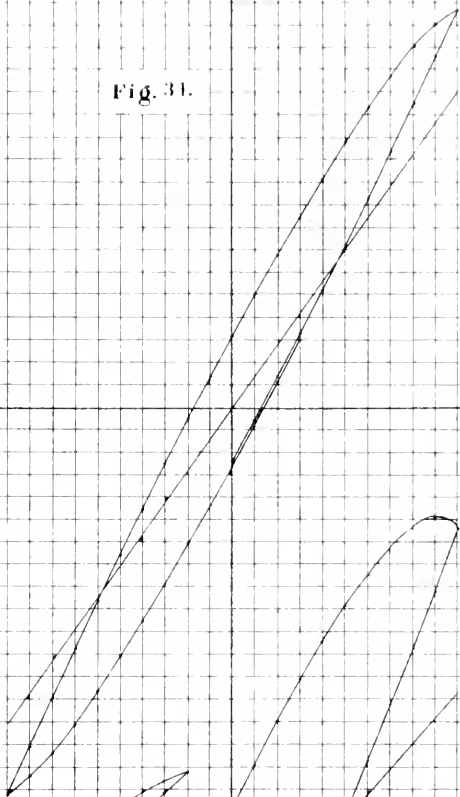


Fig. 32.

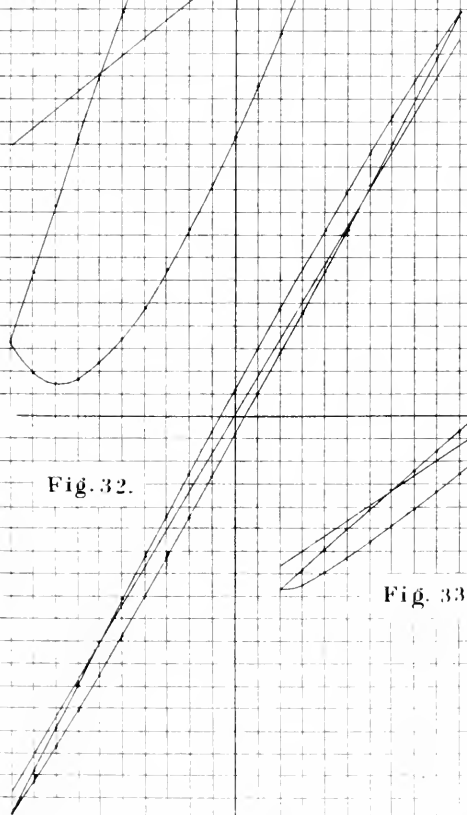


Fig. 33.

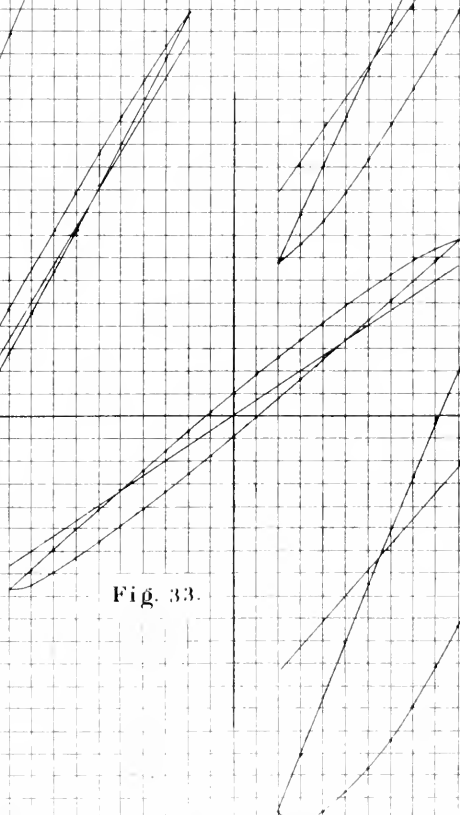


Fig. 30.

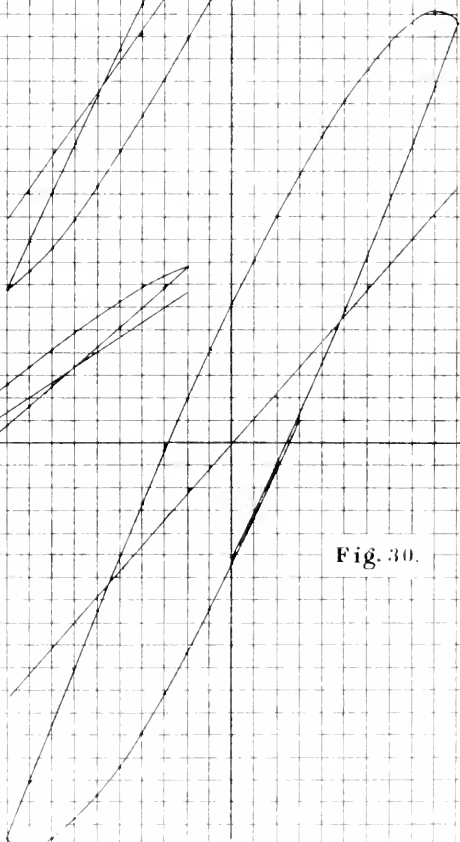




Fig. 34.  
No. 33.  
Sandstone.

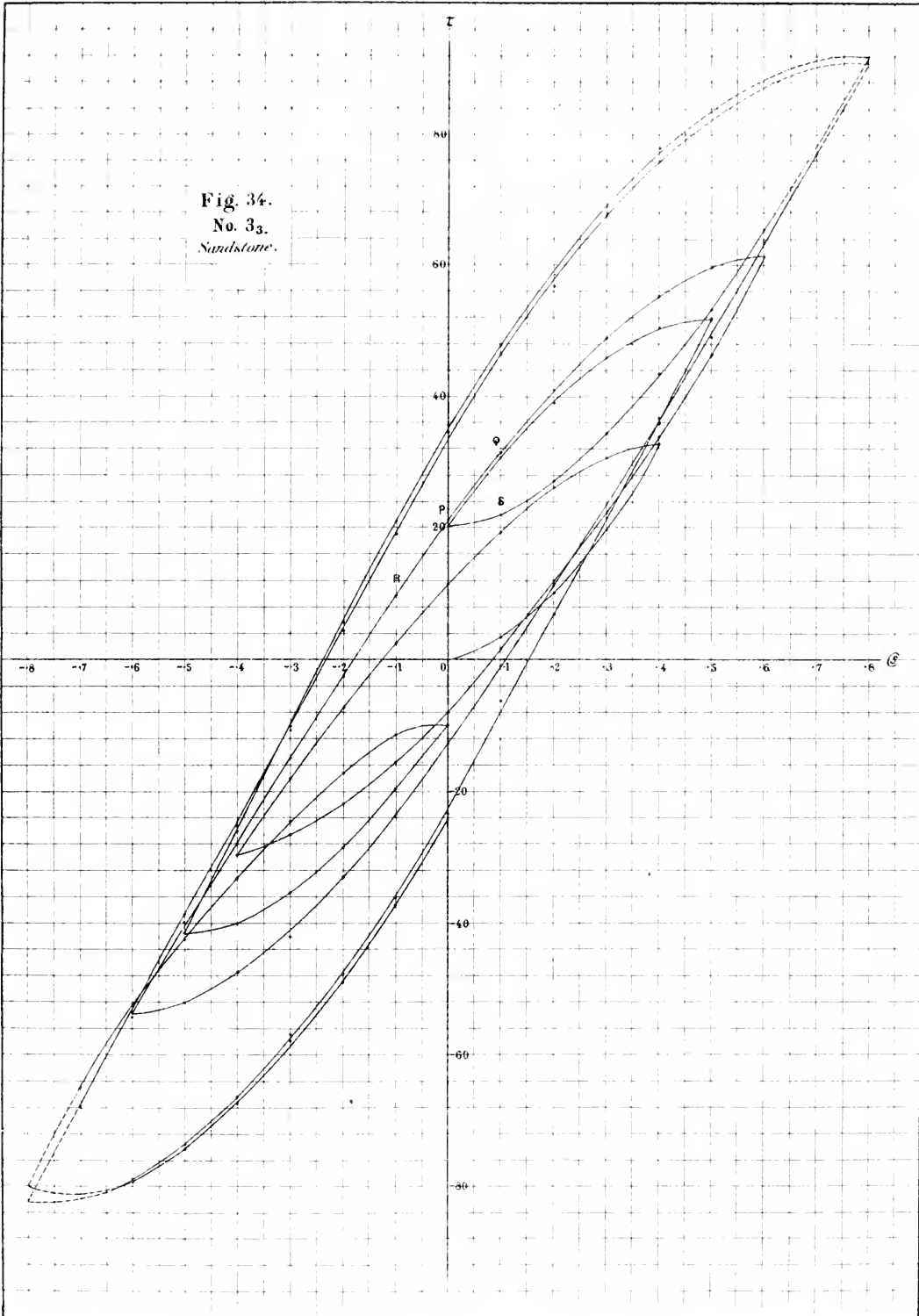




Fig. 35.  
No. 32.  
*Sandstone.*

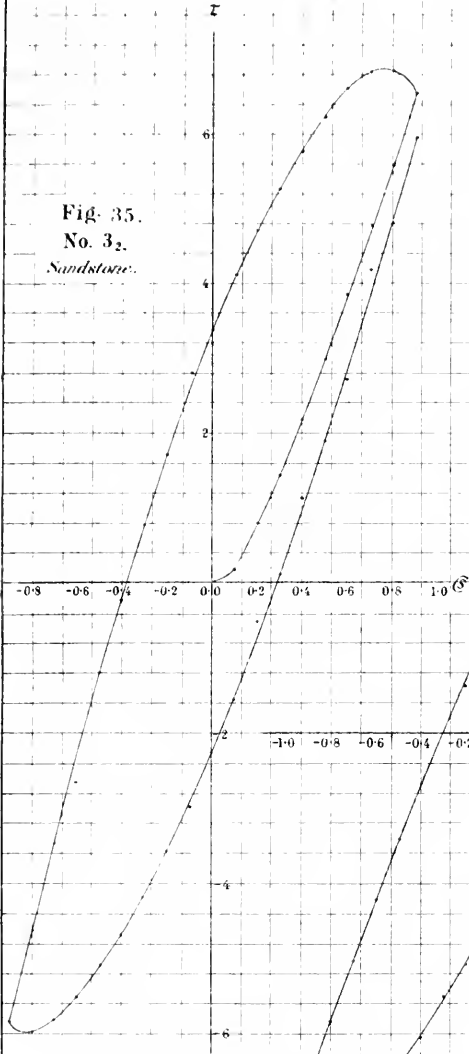


Fig. 36.  
No. 31.  
*Sandstone.*

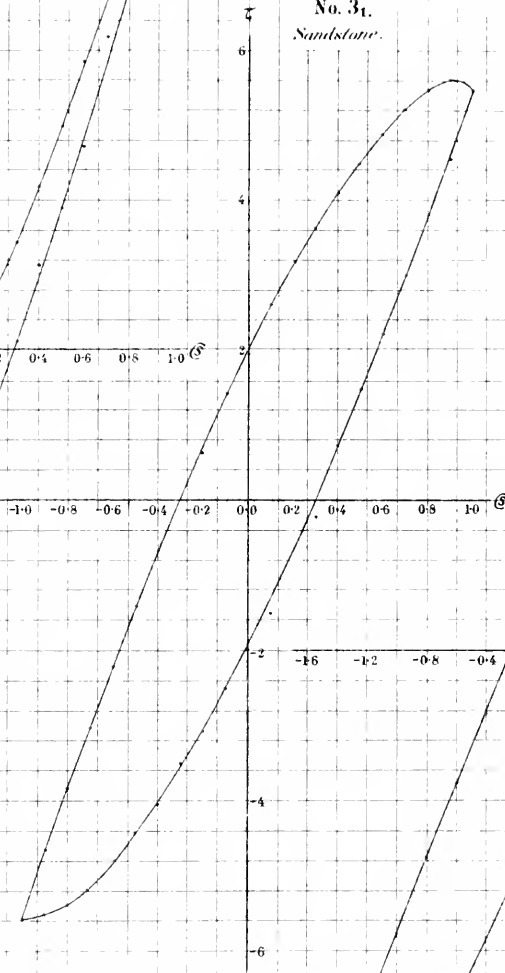
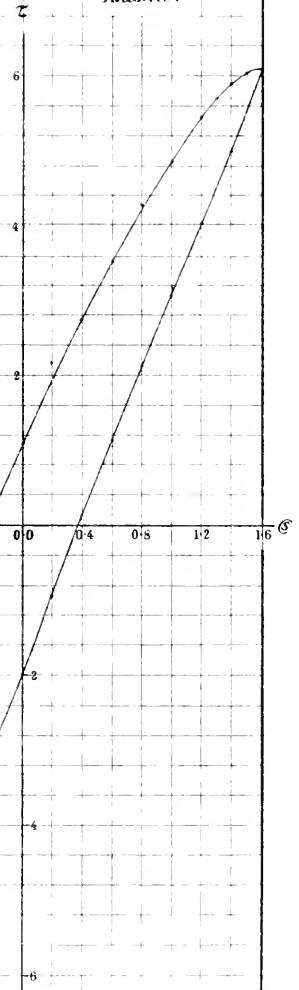


Fig. 37.  
No. 52.  
*Rhyolite.*





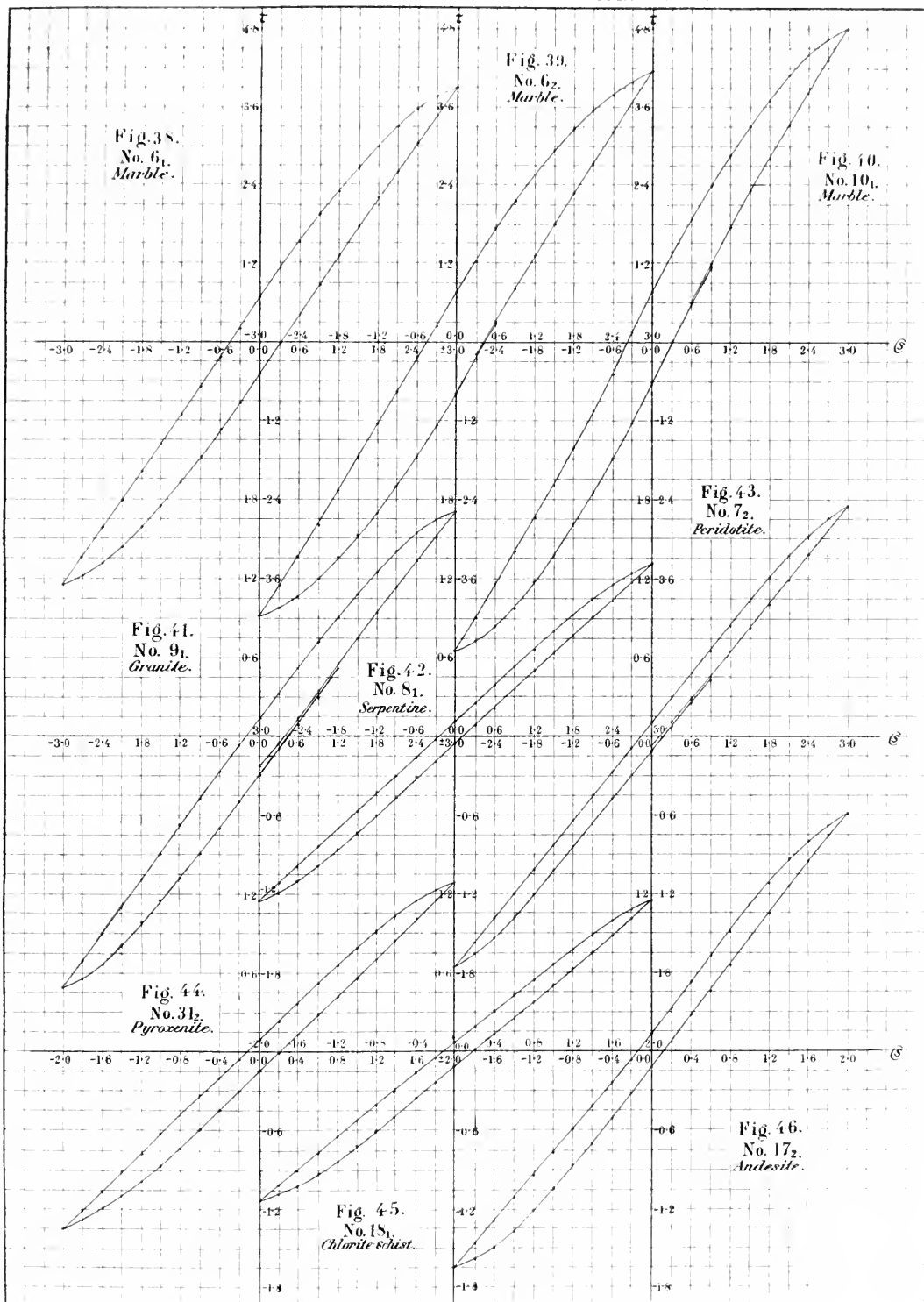






Fig. 47.  
No. 33.  
*Sandstone.*

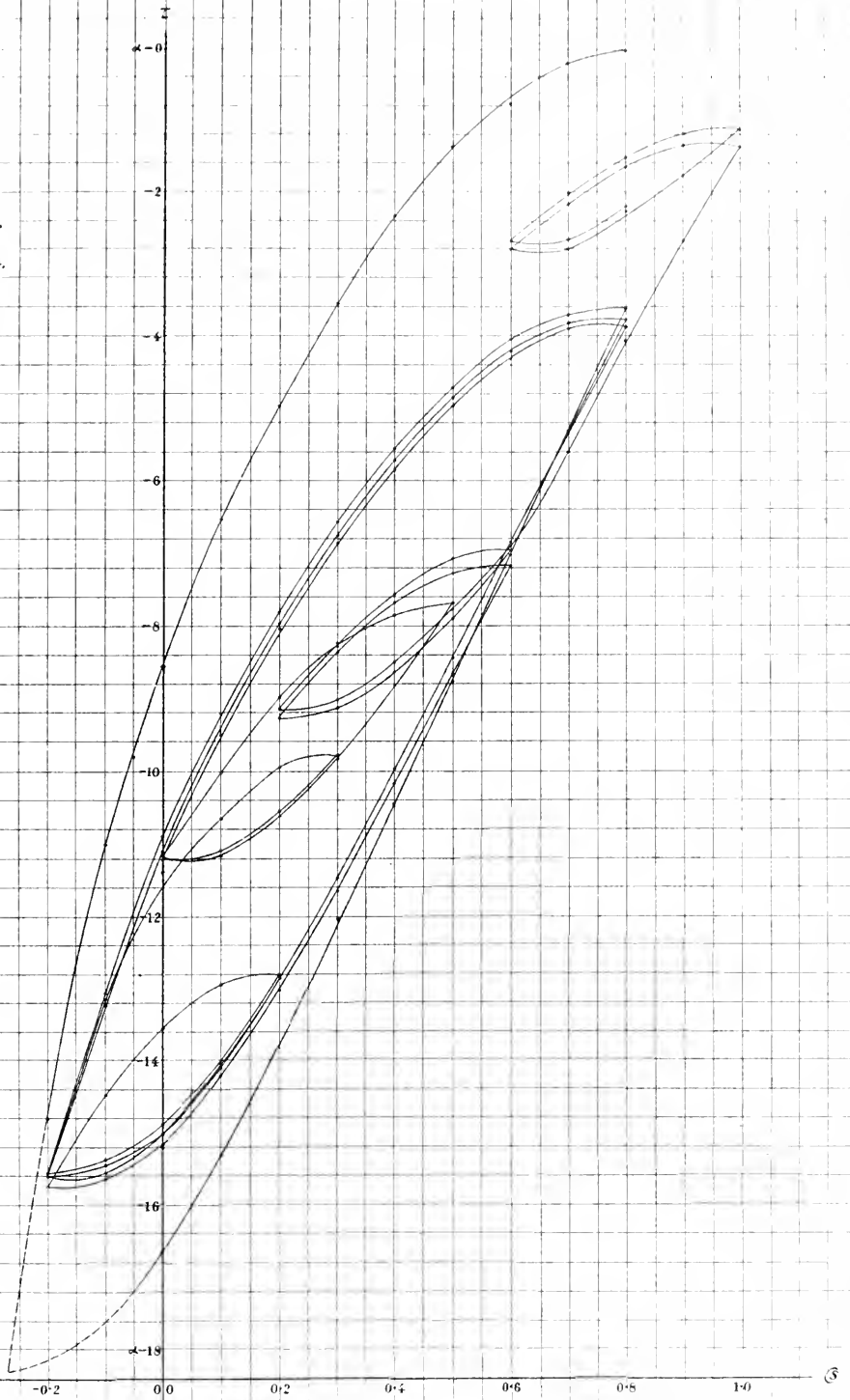




Fig. 48.  
No. 161.  
*Andesite.*

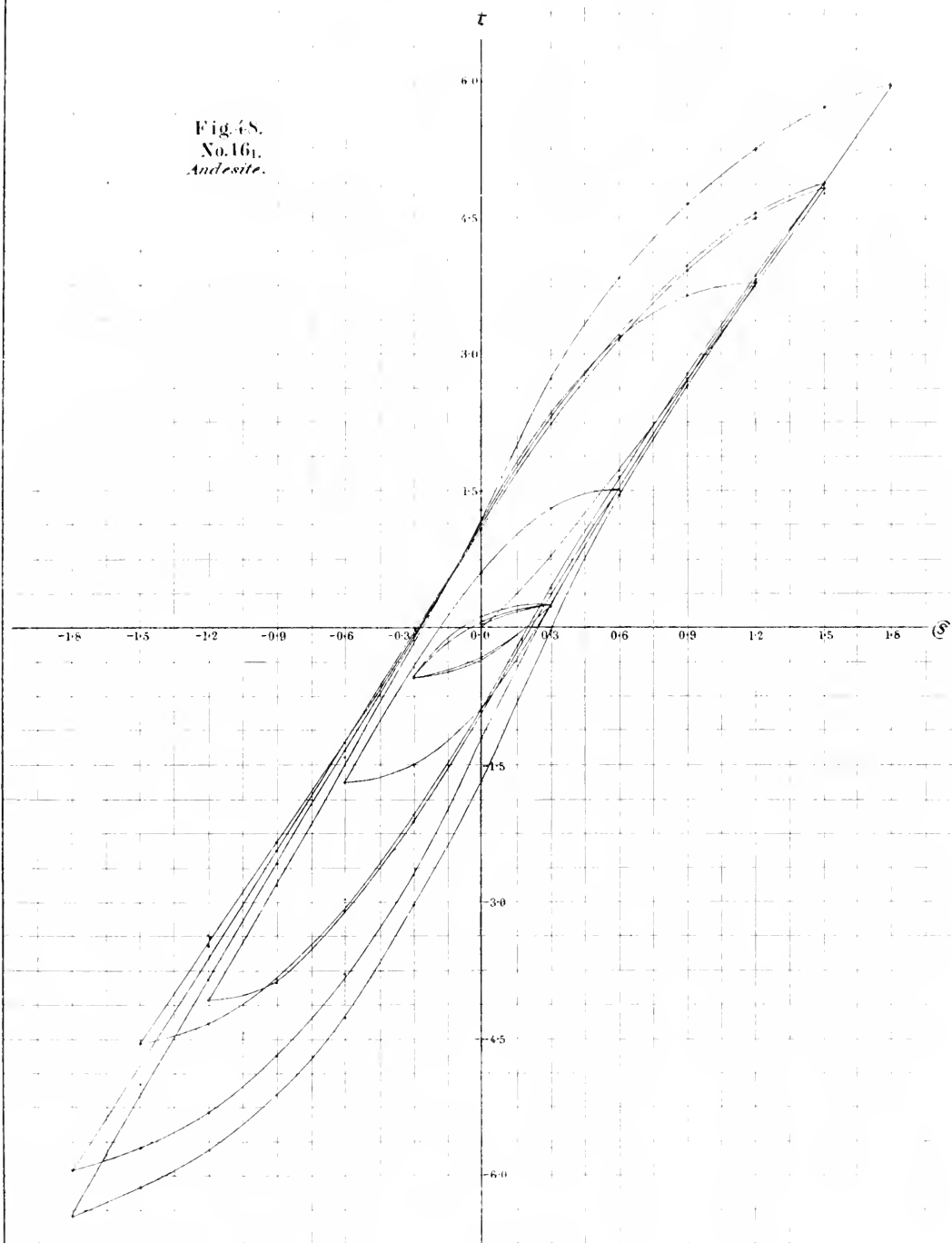
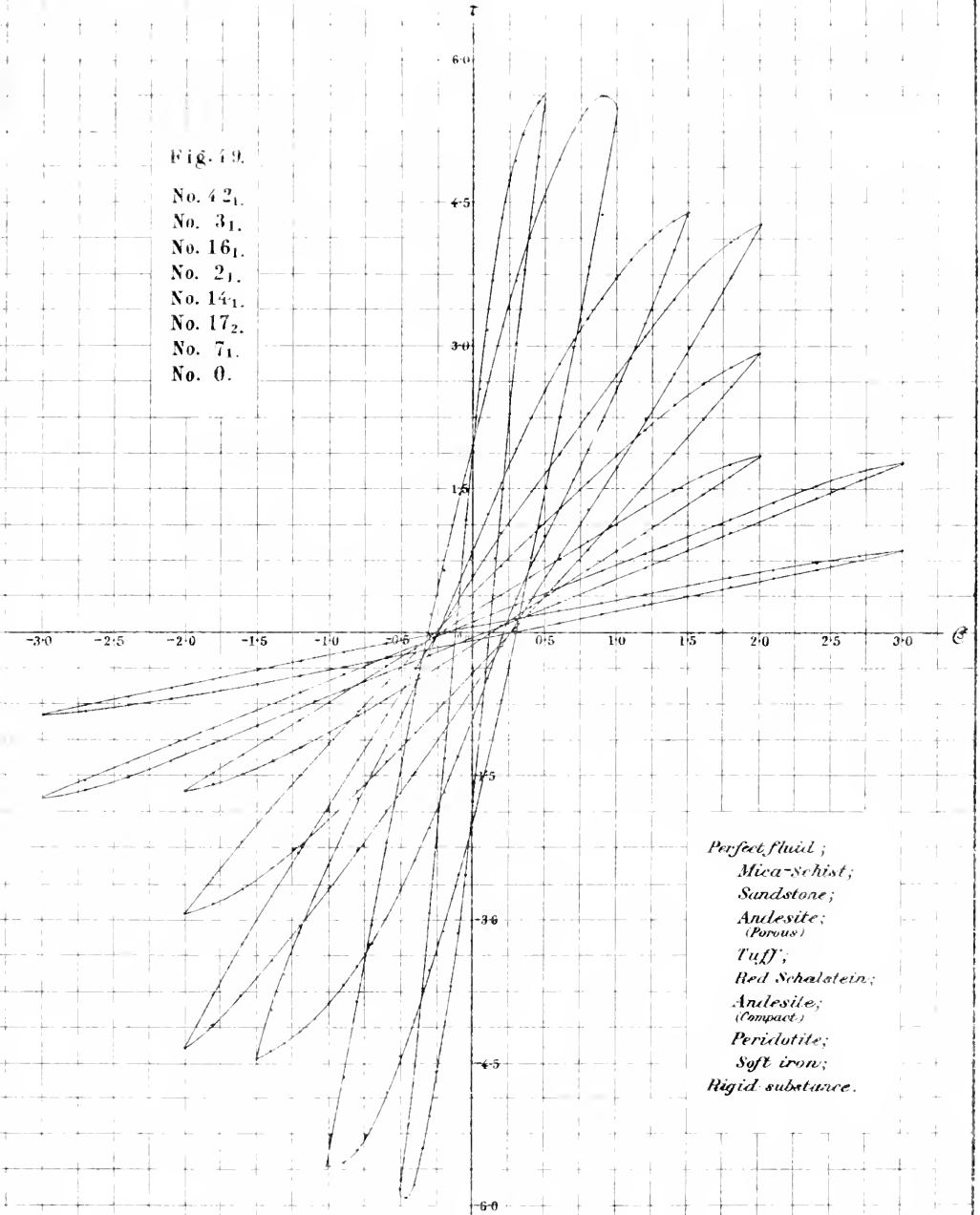




Fig. 19.

No. 4<sub>1</sub>.  
No. 3<sub>1</sub>.  
No. 16<sub>1</sub>.  
No. 2<sub>1</sub>.  
No. 14<sub>1</sub>.  
No. 17<sub>2</sub>.  
No. 7<sub>1</sub>.  
No. 0.



*Perfect fluid ;  
Mica-schist ;  
Sandstone ;  
Andesite ;  
(Porous)  
Tuff ;  
Red Schalstein ;  
Andesite ;  
(Compact)  
Peridotite ;  
Soft iron ;  
Rigid substance.*



Fig. 50.

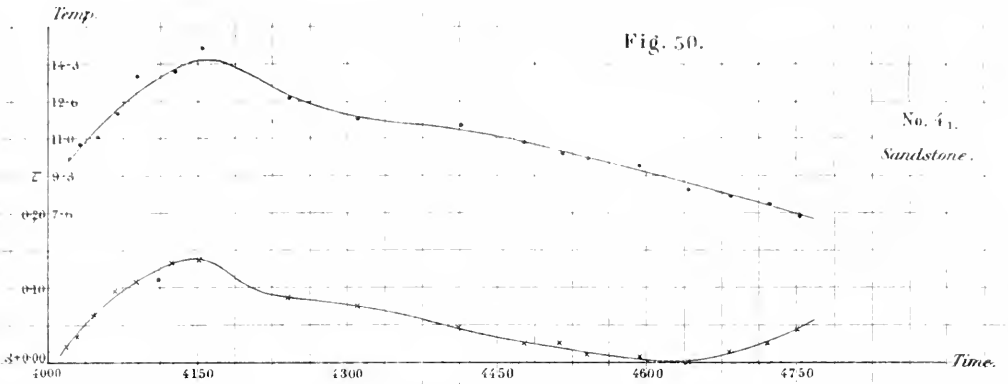


Fig. 51.

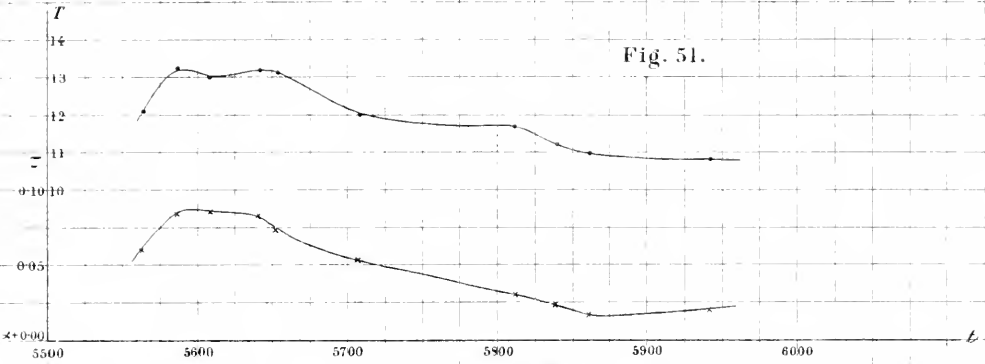


Fig. 52.

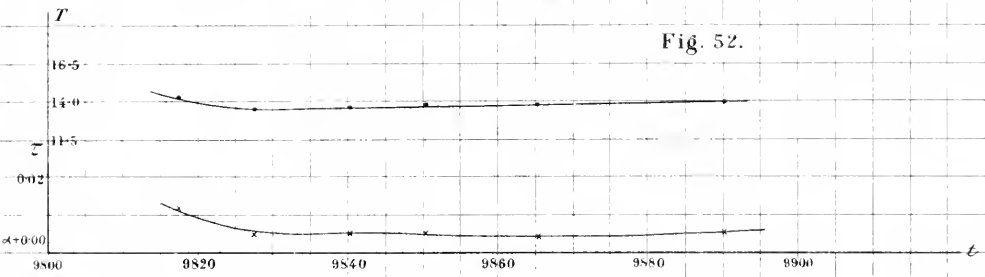
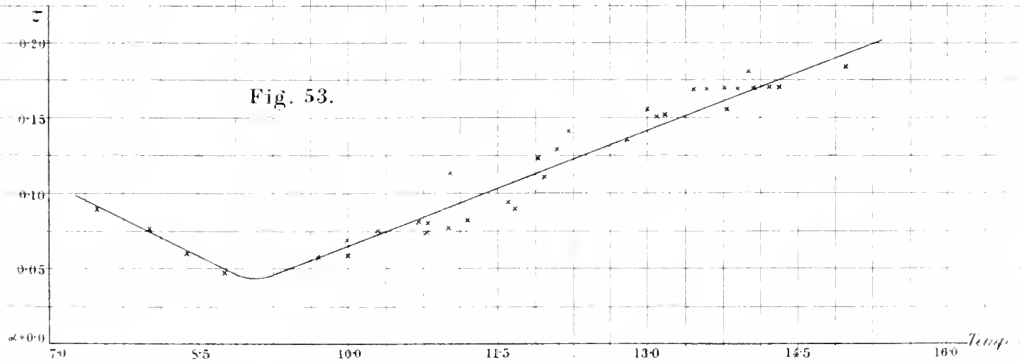


Fig. 53.







# Ueber einige Anhydrobasen aus Diaminen der Fettreihe:

Von

T. Haga und R. Majima.

## ERRATA.

Page	9	Line	4.	For	Pl. IV.	read	Pls. IV <sub>a</sub> and IV <sub>b</sub> .
"	11	"	last.	"	IV.	"	IV <sub>a</sub> , IV <sub>b</sub> .
"	14	"	4.	"	7 9	"	7:9.
"	18	"	12	"	reached	"	reached.
"	40	"	16.	"	con-	"	con-

us Diaminen der  
 rbindungen der  
 r den Schmelz-  
 yläthylendiamin  
 ldiamin bezw.  
 lang ihm jedoch  
 n; die Existenz  
 tin und Gold in  
 Bestimmung des  
 geführt. Einige  
 hode zur Gewin-

nung dieser Anhydrobasen durch trockne Destillation eines Gemisches von salzsaurem Diamin und Natriumacetat. Mit Hilfe dieses Processes stellte er Aethenyldiamin dar, das er Lysidin nannte, auf Grund seines bemerkenswerthen Verhaltens, ein sehr leicht lösliches Harnsäuresalz zu bilden<sup>2)</sup>. Seine Schüler G. Baumann<sup>3)</sup> und E. Klingenstein<sup>4)</sup> haben

<sup>1)</sup> Ber. d. D. ch. G. **21**, 2332 (1888).

<sup>3)</sup> Ber. d. D. ch. G. **28**, 1176 (1895).

<sup>2)</sup> Ber. d. D. ch. G. **27**, 2952 (1891).

<sup>4)</sup> Ber. d. D. ch. G. **28**, 1173 (1895).



## Ueber einige Anhydrobasen aus Diaminen der Fettreihe:

Von

T. Haga und R. Majima.

A. W. Hofmann hat zuerst die Anhydrobasen aus Diaminen der Fettreihe in der Weise dargestellt, dass die Diacetylverbindungen der Letzteren in einem Strom trocknen Salzsäuregases über den Schmelzpunkt erhitzt wurden<sup>1)</sup>. Er hat dadurch aus Diacetyläthylendiamin und Diacetyltrimethylendiamin Aethylenäthyldiamin bzw. Trimethylenäthyldiamin gewonnen. Es gelang ihm jedoch nicht, das Letztere im reinen Zustand isolirt zu erhalten; die Existenz desselben wurde nur durch die Bestimmung von Platin und Gold in den Doppelchloriden bewiesen. Er hat ferner keine Bestimmung des Stickstoffs oder des Kohlenstoffs und Wasserstoffs ausgeführt. Einige Jahre später publicirte A. Ladenburg eine neue Methode zur Gewinnung dieser Anhydrobasen durch trockne Destillation eines Gemisches von salzsaurem Diamin und Natriumacetat. Mit Hilfe dieses Processes stellte er Aethenyldiamin dar, das er Lysidin nannte, auf Grund seines bemerkenswerthen Verhaltens, ein sehr leicht lösliches Harnsäuresalz zu bilden<sup>2)</sup>. Seine Schüler G. Baumann<sup>3)</sup> und E. Klingenstein<sup>4)</sup> haben

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<sup>1)</sup> Ber. d. D. ch. G. **21**, 2332 (1888).

<sup>2)</sup> Ber. d. D. ch. G. **27**, 2952 (1894).

<sup>3)</sup> Ber. d. D. ch. G. **28**, 1176 (1895).

<sup>4)</sup> Ber. d. D. ch. G. **28**, 1173 (1895).

nachher auf diese Weise Dimethyl- und Methyl-äthyl-Glyoxalidin, sowie Aethyl- und Propyl-Glyoxalidin gewonnen. Dieselbe Methode wurde seitdem durch den Einen von uns, gemeinschaftlich mit C. Harries, auf 2.4-Diaminopentan ausgedehnt, mit genügender Ausbeute an den entsprechenden Anhydrobasen, deren Nitrats sich als leicht krystallisirbar und demgemäss zur Isolirung der Basen besonders geeignet erwiesen<sup>5)</sup>. Wir kamen nun auf den Gedanken, dass auch Trimethylenäthyldiamin wahrscheinlich ein gut krystallisirbares Nitrat liefere, sodass es ein bequemes Mittel zur Gewinnung von Trimethylenäthyldiamin in reinem Zustand aus salzsaurem Trimethyldiamin abgeben könnte. Die Ergebnisse unserer Experimente bestätigten diese Erwartung. Die Ausbeute war jedoch nicht so befriedigend wie wir erwarteten, und entsprach nur etwa 50 pCt. der theoretischen; dabei trat Diacetyltrimethyldiamin als hauptsächlichstes Nebenproduct auf. Während im Falle des Glyoxalidins keine Angaben über die entsprechende Diacetylverbindung gemacht wurden, haben G. Baumann und E. Klingenstein die Bildung der Diacetyldiamine bei der Darstellung der Homologen des Glyoxalidins stets beobachtet. Wir bemerkten die interessante Thatsache, dass auch harnsaures Trimethylenäthyldiamin in Wasser auffällenderweise leicht löslich ist. Wir haben ferner die Gewinnung der Anhydrobase aus Tetramethyldiamin mittels der oben angeführten Methode versucht und vermochten dieselbe ebenfalls zu erhalten. Der Ertrag ist leider noch spärlicher, weil Diacetyltetramethyldiamin das Hauptproduct der Reaction bildet. Alle diese Thatsachen machen, wie uns scheint, die Annahme wahrscheinlich, dass bei der Methode Ladenburgs Monoacetyldiamin als Zwischenproduct auftrat, indem ein Theil desselben sich weiter anhydrisirte und die heterocyclische Aethenylbase erzeugte, während ein anderer Theil desselben ein additionelles

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<sup>5)</sup> Ber. d. D. ch. G. **32** 1195 [1899].

Acetylradical aufnahm und Diacetyldiamin bildete. Diese Annahme erklärt den beobachteten Unterschied in der Ausbeute bei Ladenburgs und Hofmanns Methoden. Dass man das Monoacetyldiamin nicht thatsächlich isolieren konnte, ist leicht erklärlich durch die Annahme, dass die Umwandlung dieser Verbindung in die Anhydrobase, beziehungsweise, das Diacetyldiamin sehr schnell erfolgt, und infolgedessen die Menge des Monoacetyldiamins immer sehr klein bleibt. Die Leichtigkeit, mit welcher Monoacetyldiamine in die entsprechenden Anhydrobasen übergehen, nimmt in dem Maasse ab, wie die Zahl der die Aminoradicalen trennenden Kohlenstoffatome über zwei zunimmt, während, im Gegentheil, die Bildung der Diacetyldiamine immer mehr begünstigt wird.

Salzsaures Trimethyldiamin,  $(\text{CH}_2)_3(\text{NH}_2, \text{HCl})_2$ .

Dieser Körper wurde, nach der Vorschrift von E. Fischer und Koch, durch die Einwirkung von alkoholischem Ammoniak auf Trimethylenbromid dargestellt<sup>1)</sup>. Etwa 100 g Bromid lieferten 22 g salzsaures Salz, entsprechend ca. 30 pCt. der theoretisch verlangten Menge. Es schmilzt im Capillarröhrchen bei 243°; dieser Schmelzpunkt blieb völlig constant trotz wiederholtem Abkühlen und Schmelzen. Fischer und Koch geben den Schmelzpunkt des Salzes nicht an. Andere Eigenschaften stimmten mit den Angaben E. Fischer's und Koch's gut überein.

Aethenyltrimethyldiamin( $\mu$ -Methyl-tetrahydropyrimidin),



5 g getrocknetes und gepulvertes, salzsaures Trimethyldiamin (1 Mol.) wurde innig gemischt mit 8 g frisch geschmolzenen und gepulverten Natriumacetats (3 Mol.). Das Gemisch wurde zuerst

<sup>1)</sup> Ann. d. Chem. **232**, 222.

in einer kleinen Retorte im Oelbade bis  $240^{\circ}$  Badtemperatur, und dann einige Minuten über der directen Flamme erhitzt. Schon im Bade fing der Inhalt der Retorte zu schmelzen an. Einige Cubikcentimeter der klaren Flüssigkeit wurden abdestillirt und darin unter anderen Trimethylendiamin, Essigsäure und Aceton gefunden. Beim Erhitzen über directer Flamme ging eine etwas hellbraun gefärbte Flüssigkeit über. Das Erhitzen wurde nun unterbrochen, und nach völligem Abkühlen der Inhalt der Retorte abermals unter ca. 20 mm Druck über directer Flamme der Destillation unterworfen. Das Destillat war schwach braun gefärbt, und die letzte Portion desselben erstarrte in der Seitenröhre der Retorte. Verschiedene Antheile des Destillats wurden nun vereinigt, in ein wenig Wasser gelöst und mit überschüssiger Natronlauge geschüttelt. Die braun gefärbte, ölige Schicht wurde von der alkalischen Lösung abgetrennt und unter vermindertem Druck (ca. 20 mm) destillirt. Das erste Destillat bestand aus Wasser mit Beimengung von Trimethylendiamin; ca. 5 pCt. der Letzteren liessen sich dadurch zurückgewinnen. Als die Badtemperatur auf ca.  $170^{\circ}$  stieg, ging eine Flüssigkeit über, welche sofort in der Seitenröhre des Destillirkolbens krystallisirte; daher ist es zweckmässig, die Destillation im Anschütz'schen Kolben vorzunehmen. Gegen  $200^{\circ}$  Badtemperatur hörte die Destillation auf, aber über  $270^{\circ}$  erschien eine syrupöse Flüssigkeit, die sofort in der Seitenröhre krystallisirte. Das erste Destillat, welches zwischen  $170$ — $200^{\circ}$  überging, war eine starke, etwas nach Ammoniak, riechende Base, löslich in Wasser, Alkohol, Chloroform, aber schwieriger in Aether und Benzol. Das Chlorid und Sulfat waren sehr hygroskopisch; das Nitrat krystallisirte in schönen Prismen und war völlig beständig in trockner, aber etwas hygroskopisch in feuchter Luft. Die zwischen  $170$ — $200^{\circ}$  übergehende Fraction lieferte ca. 3 g fast reinen Nitrats, entsprechend etwa 50 pCt. der theoretischen Ausbeute. Umkrystallisirt aus Wasser, zeigte es

einen Schmelzpunkt von 109—110°. Die Analyse ergab folgende Zahlen, die mit denen von salpetersaurem Aethenyltrimethylendiamin gut übereinstimmen.

0.2176 g Sbst.: 0.2988 g CO<sub>2</sub>, 0.1325 g H<sub>2</sub>O.—0.1025 g Sbst.: 22.8 ccm N (15°, 762 mm).

C<sub>5</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>. Ber. C 37.21, H 6.89, N 26.12.

Gef. » 37.45, » 6.76, » 26.09.

Die freie Base<sup>1)</sup> lässt sich aus dem Nitrat mittels concentrirter Natronlauge darstellen. Als das ausgeschiedene Oel zweimal in vacuo fractionirt wurde, lieferte es eine krystallinische Base, die unter 12 mm Druck zwischen 120—126° siedete. Sie wurde zwei Wochen lang über Baryumoxyd gehalten und zeigte dann einen Schmelzpunkt von ca. 72—74°.

0.1003 g Sbst.: 0.2256 g CO<sub>2</sub>, 0.0906 g H<sub>2</sub>O.—0.1343 g Sbst.: 32.6 ccm N (15.5°, 760.7 mm).

C<sub>5</sub>H<sub>10</sub>N<sub>2</sub>. Ber. C 61.12, H 10.27, N 28.61.

Gef. » 61.34, » 10.11, » 28.23.

Oxalat. Dieses Salz wurde in der Weise dargestellt, dass die alkoholische Lösung der Base mit in Alkohol gelöster, wasserfreier Oxalsäure versetzt und dann durch Aether gefällt wurde, wobei das Oxalat sich in schönen, seidenglänzenden Nadeln, die bei 119° schmelzen, abschied. Es ist hygroskopisch.

0.1109 g Sbst.: 0.1819 g CO<sub>2</sub>, 0.0652 g H<sub>2</sub>O.—0.1322 g Sbst.: 17 ccm N (15°, 758 mm).

C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>. Ber. C 44.63, H 6.43, N 14.92.

Gef. » 44.72, » 6.57, » 14.94.

<sup>1)</sup> Es erwies sich als unthunlich, die Chloroformlösung der Aethenylbase mit Kaliumcarbonat oder Natriumsulfat zu trocknen, weil die Base sich beim Verdunsten des Lösungsmittels nicht mehr krystallinisch abscheidet. Eine braune, zähe Masse blieb dabei zurück, aus welcher wohl hygroskopische Krystalle des Chlorides der Aethenylbase erhalten werden konnten, aber nur ein kleiner Bruchtheil der freien Base durch Destillation in vacuo zurückgewonnen wurde. Augenscheinlich fand eine Reaction zwischen der Base und Chloroform statt.

Pikrat. Versetzt man die etwas concentrirte, alkoholische Lösung der Base mit einer ebenfalls concentrirten, alkoholischen Pikrinsäurelösung, so entstehen gelbe, abgeplattete Prismen des Pikrates, welche bei  $152^{\circ}$  schmelzen und sich leicht in heissem, schwieriger in kaltem Wasser lösen.

0.1414 g Sbst.: 24.7 ccm N ( $8^{\circ}$ , 768 mm).

$C_{11}H_{13}N_5O_7$ . Ber. N 21.50. Gef. N 21.22.

Chloroplatinat. Dieses Salz ist in Wasser löslich; es krystallisirt in orange gefärbten, kurzen Prismen, die bei  $206\text{--}207^{\circ}$  unter Zersetzung schmelzen.

0.1222 g Sbst.: 0.0391 g Pt.

$C_{10}H_{22}N_4PtCl_6$ . Ber. Pt 32.2. Gef. Pt 32.0.

Harnsäuresalz. Die wässrige Lösung der Base löst eine erhebliche Menge Harnsäure. Von dieser wurde so viel zugesetzt, dass sie sich nicht mehr löste, dann filtrirt und das Filtrat in einem Vacuumexsiccator abgedunstet. Eine weisse, pulvrige Substanz blieb zurück, welche, aus Alkohol umkrystallisirt, in Form von kleinen Octaëdern erhalten wurde. Das Salz ist in weniger als 4 Theilen Wasser löslich.

0.1258 g Sbst.: 33.3 ccm N ( $13^{\circ}$ , 765 mm).

$C_{10}H_{14}N_6O_3$ . Ber. N 31.63. Gef. N 31.53.

Diacetyl-trimethyldiamin,  $(CH_3)_3(NH.COCH_3)_2$ .

Das zweite, bei über  $270^{\circ}$  Badtemperatur übergehende Destillat wog 0.6 g. Es ist neutral gegen Reagenspapier und löslich in Wasser, Alkohol und Chloroform, unlöslich in Aether. Es krystallisirt aus Alkohol in kleinen Prismen, die bei  $101^{\circ}$  schmelzen. Die Analyse führte zu folgenden Zahlen; übereinstimmend mit denen für Diacetyl-trimethyldiamin:

0.1332 g Sbst.: 0.2610 g  $CO_2$ , 0.1067 g  $H_2O$ .—0.1260 g Sbst.: 19.6 ccm N ( $15^{\circ}$ , 746 mm).



$C_7H_{11}O_2N_2$ . Ber. C 53.16, H 8.98, N 17.72.

Gef. » 53.44, » 8.86, » 17.78.

H. Strache<sup>1)</sup> beschrieb früher diesen Körper und gab den Schmelzpunkt zu 79° an. Um diese grosse Differenz in den Schmelzpunkten aufzuklären, haben wir die Substanz nach der vom genannten Autor benutzten Methode dargestellt, d. h. durch mehrstündiges Kochen von Trimethyldiamin mit überschüssigem Essigsäureanhydrid. Wir haben hierbei eine Substanz erhalten, die im Schmelzpunkt und ihren sonstigen Eigenschaften mit unserem eigenen Präparat vollkommen übereinstimmte. Wir sind daher geneigt anzunehmen, dass die Zahl H. Strache's nicht richtig ist. Möglicherweise dürfte hier ein Druckfehler vorliegen.

Diacetyltrimethyldiamin ist schwach basisch und giebt ein krystallinisches Oxalat, wenn man die alkoholische Lösung mit in Alkohol gelöster, wasserfreier Oxalsäure versetzt und mit Aether fällt. Es krystallisirt in kurzen Nadeln, die bei 126° schmelzen.

0.1555 g Sbst : 0.2490 g  $CO_2$ , 0.0925 g  $H_2O$ .—0.1608 g Sbst.: 16.5 ccm N (21°, 750 mm).

$C_7H_{16}N_2O_6$ . Ber. C 43.51, H 6.50, N 11.31.

Gef. » 43.67, » 6.61, » 11.46.

Wir haben noch eine Darstellung von Aethenyltrimethyldiamin nach der von Hofmann befolgten Methode ausgeführt, um zu sehen, ob dabei die Ausbeute besser ausfällt, als nach der Methode Ladenburgs.

Diacetyltrimethyldiamin wurde auf 180° erhitzt und durch die geschmolzene Masse trocknes Salzsäuregas drei Stunden lang hindurchgeleitet. Concentrirte Natronlauge wurde dann zum abgekühlten Retorteninhalt zugesetzt und das ausgeschiedene, von der alkalischen Lösung abgetrennte Oel sofort der Destillation unterworfen. Das

<sup>1)</sup> Ber. d. D. ch. G, **21**, 2365 (1888).

erste Destillat bestand aus Aethenylbasen, deren Ausbeute nach Ueberführung in das Nitrat etwa 30 pCt. der theoretischen betrug. Die Methode ist also gut brauchbar, obschon sie entschieden dem Verfahren Ladenburgs nachsteht. Der letzte Antheil des Destillats enthielt Beimengungen von anderen basischen Substanzen, unter welchen sich ein Körper vorfand, der ein in Alkohol schwer lösliches und bei  $141^{\circ}$  schmelzendes Oxalat lieferte. Dieser konnte wegen zu geringer Menge leider nicht näher untersucht werden.

Diacetyltetramethyldiamin,  $(\text{CH}_2)_4(\text{NH}\cdot\text{COCH}_3)_2$ .

Nachdem uns bei einem  $\alpha,\gamma$ -Diamine die Darstellung der Anhydrobasen ohne Schwierigkeit gelungen war, erschien es uns von einigem Interesse, zu untersuchen, ob  $\alpha,\delta$ -Diamine, z. B. Tetramethyldiamin, bei ähnlicher Behandlung ebenfalls Anhydrobasen erzeugen.

Tetramethyldiamin wurde, nach dem Vorgange Ladenburgs, durch Reduction von Aethylencyanid in alkoholischer Lösung mittels metallischen Natriums dargestellt<sup>1)</sup>. Das salzsaure Salz dieser Base wurde mit Natriumacetat zum Schmelzen erhitzt, ganz in gleicher Weise, wie bei dem salzsauren Trimethyldiamin angegeben worden ist. Ein klares Destillat, welches ein wenig Diamin enthielt, ging über, und beim Abkühlen traten grosse, krystallinische Streifen an der Wand des Kolbens nahe über der geschmolzenen Masse auf. Als das Erhitzen des Kolbens unter ca. 12 mm Druck über directer Flamme fortgesetzt wurde, destillirte eine syrupöse Flüssigkeit ab, die sofort im Hals der Retorte zu Krystallen erstarrte. Die Letzteren, mit ein wenig Wasser aufgenommen und mit concentrirter Natronlauge behandelt, schieden ein Oel ab, das aber sofort krystallisirte. Die alkalische Lösung wurde abfiltrirt und die Krystalle auf Thon ge-

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<sup>1)</sup> Ber. d. D. ch. G. **19**, 780 (1886).

trocknet. Diese Verbindung ist in Wasser und Alkohol löslich, nicht aber in Aether. Löslich ist sie auch in heissem Chloroform, weniger in kaltem. Aus Wasser umkrystallisiert, erscheint sie in Form kleiner Prismen vom Schmelzpunkt  $137^{\circ}$ , die gegen Reagenspapier neutral sind. Die Menge betrug ca. 1.1 g. Die Analyse einer einen Tag im Vacuumexsiccator getrockneten Probe bewies, dass Diacetyltetramethyldiamin vorlag.

0.1285 g Stbst.: 0.2628 g  $\text{CO}_2$ , 0.1031 g  $\text{H}_2\text{O}$ .—0.1415 g Stbst.: 19.4 ccm N ( $11^{\circ}$ , 757.5 mm).

$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2$ . Ber. C 55.75, H 9.36, N 16.31.

Gef. » 55.78, » 8.98, » 16.22.

Aethenyltetramethyldiamin,  $(\text{CH}_2)_4\text{N}^+\text{CCH}_3$ .

Da die Krystallisation des Aethenyltetramethyldiamins augenscheinlich schwierig ist, während das Diacetyltetramethyldiamin leicht krystallisiert, wurde der Thon, auf welchem das Letztere entwässert worden war, mittels Wasser ausgezogen. Die so erhaltene Lösung wurde in vacuo bei einer Temperatur von  $40\text{--}45^{\circ}$  abgedunstet. Der zähe Rückstand wurde mit concentrirter Natronlauge behandelt und das dabei ausgeschiedene Oel in einem kleinen Destillirkolben unter 12 mm Druck destillirt. Zuerst gingen Wasser und Tetramethyldiamin über, dann folgte gegen  $220^{\circ}$  Badtemperatur eine syrupöse Flüssigkeit, die beim Neutralisiren mit Salzsäure und Zusatz von Goldchlorid ein gut krystallisirtes, salzsaures Golddoppelsalz lieferte. Dieser letztere Körper ist in heissem Wasser löslich, aber weniger in kaltem, und krystallisiert aus Wasser in kleinen Prismen, deren Schmelzpunkt bei  $157^{\circ}$  liegt.

0.1608 g Stbst.: 0.0692 g Au.

$\text{C}_6\text{H}_{12}\text{N}_2\text{H}[\text{AuCl}_4]$ . Ber. Au 43.6. Gef. Au 43.1.

Das salzsaure Platindoppelsalz dieser Base ist in Wasser sehr leicht löslich.

0.0649 g Subst.: 0.0195 g Pt.

$2 \text{ C}_6\text{H}_{12}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ . Ber. Pt 30.7. Gef. Pt 30.1.

Wir haben ferner eine kleine Menge von freier Aethenylbase isolirt, welche durch die fractionirte Destillation in vacuo direct von Diacetyltetramethylen-diamin abgetrennt wurde. Jedoch konnten wir die freie Base wegen der geringen Ausbeute nicht näher studieren. Wir waren dennoch im Stande, das Pikrat darzustellen und eine vollständige Analyse desselben auszuführen, welche eine weitere Bestätigung unserer Ergebnisse lieferte. Das Pikrat ist sehr leicht in Wasser und Alkohol löslich und krystallisirt aus dem Letzteren in kurzen Prismen, welche bei  $138^\circ$  schmelzen.

0.1031 g Subst.: 0.1531 g  $\text{CO}_2$ , 0.0380 g  $\text{H}_2\text{O}$ .—0.1024 g Subst.: 17.3 ccm N ( $16^\circ$ , 760 mm).

$\text{C}_6\text{H}_{12}\text{N}_2$ ,  $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ . Ber. C 40.99, H 4.30, N 19.98.

Gef. » 40.50, » 4.12, » 19.62.



## On the Diffusion of Liquids.

By

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§1. The first thorough experimental study of the free diffusion of liquids was made by Graham<sup>(1)</sup> in 1850—1861, and soon after Fick<sup>(2)</sup> developed a theory of the free diffusion of an aqueous solution of salt under the supposition that it obeys a law analogous to the conduction of heat. When the concentration  $u$  depends simply on time  $t$  and a coordinate  $x$ , then Fick assumed that the quantity of salt  $dS$  which passes through a cross section having an area equal to  $q$  and perpendicular to the axis of  $x$  during the time  $dt$  is proportional to  $q \cdot dt$  and the gradient of the concentration  $\frac{\partial u}{\partial x}$ ; or

$$dS = kq \cdot dt \cdot \frac{\partial u}{\partial x} \quad (1)$$

where  $k$  is a constant depending on the nature of the solution and is called the constant of diffusion. It is easy to deduce from (1) the following differential equation satisfied by  $u$ ,

$$\frac{\partial u}{\partial t} = k \frac{\partial^2 u}{\partial x^2} \quad (2)$$

Several experiments were conducted to test Fick's equation and

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(1) Graham, Phil. Mag. [4] 3. 1862.

(2) Fick, Pogg. Ann. 94. 1855.

to determine the numerical value of  $k$  for various substances. The methods employed may be divided into two classes. In the first class, the quantity of salt which passed through a given section during a finite time was determined. To the second class belong those methods in which the concentrations at different depths were determined; the latter methods are preferable to the former, for they give us clear information respecting the state of the diffusing liquid at any given instant. A variety of methods were used by different experimenters. Graham, Beez,<sup>(1)</sup> Beilstein,<sup>(2)</sup> Schuhmeister<sup>(3)</sup> and others determined the quantity of salt passed through, or the concentration at any point, from the density of the liquid; Graham, and Wroblewski<sup>(4)</sup> by evaporating the water out of the solution and weighing the salt left behind. Long<sup>(5)</sup> and Scheffer<sup>(6)</sup> used titrimetrical methods. Wild and Simmler<sup>(7)</sup> who soon after the publication of Fick's paper, integrated his equation, said that the concentration at any point could be determined by a saccharimeter in the case of sugar. Hoppe-Seyler<sup>(8)</sup> and Vait<sup>(9)</sup> used this method. Wroblewski<sup>(10)</sup> and Wiedeburg<sup>(11)</sup> used the photometrical method in colored solutions. Johannisjauz,<sup>(12)</sup> at the suggestion of Kundt, used a liquid prism filled with the diffusing liquid and determined the index of refraction at different heights. Weber<sup>(13)</sup> employed an electrical method for determining the difference

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(1) Beez, *Schlömilch Zeits.* IV.

(2) Beilstein, *Ann. d. chemie u. Pharm.* 99.

(3) Schuhmeister, *Sitzungsber. d. k. Akad. d. Wissensch. zu Wien* 79.

(4) Wroblewski, *Wied. Ann.* 7.

(5) Long, *Wied. Ann.* 9.

(6) Scheffer, *Zeits. für phys. Chemie*, 2.

(7) Wild and Simmler, *Pogg. Ann.* 100, 1857.

(8) Hoppe-Seyler, *Medicinisch-chemische Untersuchungen*, 1866.

(9) Vait, *Pogg. Ann.* 130, 1867.

(10) Wroblewski, *loc. cit.*

(11) Wiedeburg, *Wied. Ann.* 41, 1890.

(12) Johannisjauz, *wied. Ann.* 2, 1877.

(13) Weber, *Wied. Ann.* 7, 1879.

of concentrations at two given points. It will be seen that, of these methods the optical and the electrical are better suited for our purpose, because if we use these methods, the liquid is not disturbed and we can day after day study how the diffusion is progressing, and get a clear insight into the phenomena. Optical methods, however, have one defect in common, as was first pointed out by Stefan.<sup>(1)</sup> His objection was that as the liquid is diffusing, the medium is un-homogeneous and consequently a ray of light meant to be sent along a given layer horizontally is curved out of that layer and tends toward that side which is optically rare, so that the concentration deduced from that experiment does not correspond to that of the layer in question. Wiener,<sup>(2)</sup> however, availed himself of this very fact, and devised an arrangement which could be used in the determination of  $k$  and also of the conductivity of heat in liquids.

The constant of diffusion  $k$  is not an absolute constant. It is a function of temperature and increases with it. It is also highly probable that it depends on the concentration. This was noticed by Graham, Wroblewski, Weber and Schuhmeister in  $\text{ZnSO}_4$  and  $\text{NaCl}$  solutions, though their results do not agree with one another. It can be easily shown that when  $k$  is variable, the differential equation for  $u$ , is

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial x} \left( k \frac{\partial u}{\partial x} \right) \quad (3)$$

where  $k=f(u)$ . Wiedeburg and Wiener took  $k$  as a linear function of  $u$ .

§2. My present communication relates to a new method of studying diffusion optically, which is quite free from Stefan's objection and is capable of giving an accurate value of  $k$ . I experimented upon  $\text{ZnSO}_4$  and  $\text{NaCl}$ , and found that the diffusion in these cases agrees with

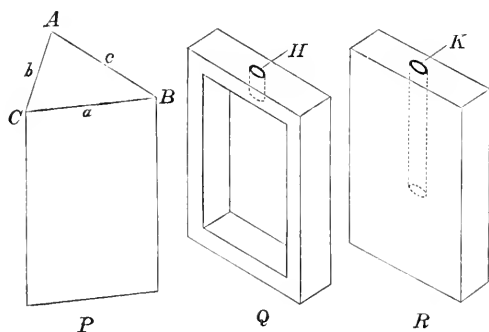
(1) Stefan, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien, 78 and 79. 1878—1879.

(2) Wiener, Wied. Ann. 49. 109. 1893.

the assumption that  $k$  is independent of  $u$ . But as my present circumstances do not allow me to repeat the experiments and confirm the results hitherto obtained, I shall not at present, insist on the last statement. Let me describe my arrangement and the method of deducing  $k$ .

In the accompanying figure 1, P is a prism glass; Q and R are made of any solid and of such size that when they are packed and pressed together slightly, the hollow space in Q, forms a closed rectangular water tight diffusion vessel bounded on one side by the prism

Fig. 1.



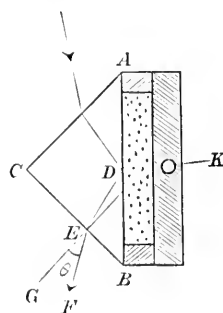
P and on the other by the plate

R. H is a hole for introducing the liquid, and is to be closed by a stopper. K is a hole bored in R, for admitting a thermometer. It does not communicate with the hollow space in Q, in order to keep the area of

the cross section of the diffusion vessel constant.

When a pencil of light is sent horizontally through the face  $b$  (fig 2) of the prism, it is reflected at the face  $c$ , where the glass is in contact with the liquid, and then emerges from the prism through the face  $a$ . When the prism is optically denser than the liquid, total reflection will take place. Let

Fig. 2.



EF be the emergent ray corresponding to the critical ray. If  $N$  and  $n$  be the indices of reflection of the glass and of the liquid respectively, and if the angle  $ABC$  of the prism be  $\alpha$  and the angle  $FEG$  be  $\theta$ , then



$$n = \sin \alpha \sqrt{N^2 - \sin^2 \theta} + \cos \alpha \sin \theta. \quad (4)$$

Now if the vessel be filled with the diffusing liquid,  $n$  and therefore  $\theta$  will be different from layer to layer. By measuring  $\theta$ , the concentration  $n$  at different heights can be deduced and  $k$  calculated.

It must be owned here that the above method involves one doubtful point. As the concentration is determined by the critical angle of total reflection, its value is that at and near the glass wall of the vessel. This may differ from the value at the interior of the liquid mass, owing to the molecular action of the wall, and the value of  $k$  deduced by this method may be influenced by the nature of the prism used. This is the point which requires further study. As I have not yet hit upon a suitable method of deciding this point, it is left as an open question (see however Wiener's paper). It may, I think, be investigated, by making the thickness of Q very small, say one-hundredth of a millimeter, and bringing the influence of the opposite wall R into the action.

This arrangement can be used as a demonstration experiment in diffusion, for the curve traced out by the critical ray EF can be projected on a screen and shown to a large audience. For this purpose, a cylindrical lens is placed in front of the face  $b$  in such a way that sun light sent toward it, is focussed at D (fig. 2) and forms there a bright vertical line. In order to avoid the heating of the liquid and the consequent convection current, an absorption trough for heat rays must be used. A long focus lens placed before the face  $a$ , will then project a curve on a screen at a proper distance. This curve consists usually of two vertical lines at its two ends connected by a curved portion having an inflexion point. This curved portion corresponds to the region where the diffusion is proceeding and the change in its form shows the progress of diffusion. Fig. 3 is from a photograph obtained by projecting the diffusion curve directly on a sensitive plate.

For the subjective experiment and for the determination of  $k$ , a different arrangement is necessary. The diffusion ves-

Fig. 3.



sel is to be furnished with adjustable tripods and placed on a spectrometer. A sodium flame is put before the face  $b$ , and directly in front of the face  $a$ , a cathetometer is placed. The telescope of the latter is provided with an auto-collimating ocular, which

is used for fixing the direction of the normal EG. When the vessel is filled with a *homogeneous* liquid, on looking through the telescope, one can at once see a sharply defined vertical boundary between the total and the partial reflections. But when the vessel is filled with the *diffusing* liquid, it is otherwise. With the full aperture of the telescope, one can not distinctly see the boundary which is curved in this case, for the evident reason that it is crossed by the vertical rays. It is necessary to cut down the rays entering the telescope to a narrow pencil in a horizontal plane. I covered the objective with a cap having a horizontal slit about 1 mm. broad, and only then was I able to see the diffusion curve distinctly. With the telescope thus furnished with a slit, it is a very simple matter to move the telescope vertically and measure the angles  $\theta$  at different heights.

In passing, it will be noticed that this method may also be used for the study of diffusion through an opaque body like sand, or through a substance like agar-agar, as investigated by Voigtländer<sup>(1)</sup>.

(1) Voigtländer, Zeits. für phys. Chemie, 3. 1889.

The experiment was conducted in the following way. The vessel was just half filled with distilled water, and then placed on the spectrometer and the verticality of the reflecting faces carefully adjusted. A glass tube drawn to a capillary in one end was introduced into the vessel so that its lower end reached the bottom of the vessel. The solution to be examined was poured very slowly, drop by drop, into the tube until the vessel was full of liquid. In this way, the solution was quietly made to occupy the lower half of the diffusion vessel. The hole H was then closed, care being taken to leave no air bubbles within the vessel. The whole was left untouched about two or three hours and then the measurement was made and repeated daily for about a week without disturbing the vessel during that time. The spectrometer and the cathetometer stood on a massive stone pier in a small room, the temperature of which never varied by more than  $2^{\circ}$  C.

§ 3. The relation between the concentration  $u$  of a salt solution and its index of refraction  $n$  is almost linear. According to Schütt,<sup>(1)</sup> the relation for NaCl solution is exactly linear. His result is given in Table I., in which  $u$  is the number of grammes of NaCl in 100 grammes of water, and  $n$  is the index of refraction for Na-light at  $18^{\circ}07$  C.

TABLE I. NaCl SOLUTION.

$u$	$n$
24.99	1.37789
19.99	1.36862
14.99	1.35959
9.99	1.35068
5.00	1.34191
3.00	1.33841
1.00	1.33491
0.30	1.33369
0.00	1.33316

(1) Schütt, Zeits. für phys. Chemie, 5, 1890.

In such cases, if we follow Fick's theory,  $n$  satisfies the differential equation (2), and there is no need of reducing  $n$  to  $u$  in calculating  $k$ . I examined the relation for  $\text{ZnSO}_4$  by Abbe's refractometer by Zeiss and found that it was not exactly linear. The result is given in Table II. In such cases, one must reduce  $n$  to  $u$  for finding the value of  $k$ .

TABLE II.  $\text{ZnSO}_4$ -SOLUTION.

$u$	$n$
71.10	1.3809
47.38	1.3696
31.92	1.3606
25.46	1.3559
21.02	1.3533
17.96	1.3509
13.95	1.3470
11.29	1.3453
9.50	1.3437
8.18	1.3427
6.40	1.3406
5.24	1.3399
4.44	1.3388
Temp. = 11.°5 C	

A solution of the equation (2) is

$$u = e^{-m^2 t} (A \sin mx + B \cos mx).$$

$m$  being a constant. In my arrangement, the diffusion vessel is rectangular and closed, its height being equal to  $H$ , and at its top and bottom  $\frac{\partial u}{\partial x}$  is equal to zero. Taking the origin of coordinate at the bottom of the vessel, the boundary conditions are, therefore,

$$\begin{aligned} \text{at } x=0, \quad \frac{\partial u}{\partial x} &= 0 \\ \text{,, } x=H, \quad \frac{\partial u}{\partial x} &= 0 \end{aligned}$$

which give us at once

$$A=0$$

$$\text{and} \quad m = \frac{p\pi}{H}, \quad p = [0, 1, 2, 3, \dots],$$

Thus  $u$  is given by

$$u = B_0 + B_1 e^{-\frac{\pi^2}{H^2}kt} \cos \frac{\pi x}{H} + B_2 e^{-\frac{4\pi^2}{H^2}kt} \cos \frac{2\pi x}{H} + \dots \quad (5)$$

Hence it follows that at  $t=0$ ,

$$u_0 = B_0 + B_1 \cos \frac{\pi x}{H} + B_2 \cos \frac{2\pi x}{H} + \dots \quad (6)$$

and at any time  $t$ ,  $u$  may be put as

$$u = b_0 + b_1 \cos \frac{\pi x}{H} + b_2 \cos \frac{2\pi x}{H} + \dots \quad (6')$$

where  $b_0 = B_0$ ,

$$b_1 = B_1 e^{-\frac{\pi^2}{H^2}kt},$$

$$b_2 = B_2 e^{-\frac{4\pi^2}{H^2}kt},$$

.....

Thus we get

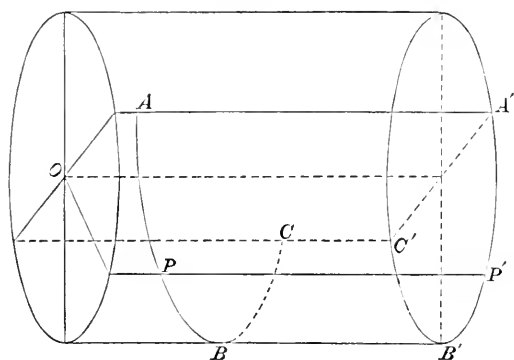
$$k = \frac{H^2}{\pi^2 t} \log_e \left( \frac{B_1}{b_1} \right) = \frac{H^2}{4\pi^2 t} \log_e \left( \frac{B_2}{b_2} \right) = \dots \quad (7)$$

Though  $k$  may be determined by any of these relations, the first relation is best suited for the purpose. In fact, when the vessel is filled with the salt solution nearly to the height  $\frac{H}{2}$  initially the coefficients  $b_2, b_3, \dots$  become within two or three days so very small that they are of no practical use in the calculation.

The expansions (6) and (6') are Fourier's series. Their coefficients may be calculated by the ordinary method of multiplying  $\cos \frac{\pi x}{H}$ ,  $\cos \frac{2\pi x}{H}$ , &c into  $u$  and integrating them, or by using harmonic analysers; but in the present case, it is more convenient to proceed as follows.

Let us suppose that we take a right circular cylinder of radius  $r$  with its axis horizontal. Draw a curve with  $u$  as the abscissa and  $x$  as the ordinate. The scale of the abscissa may be any whatsoever, but that of the ordinate must be so taken that when the curve is wrapped round the cylinder, it covers just half its surface. Let  $OA'A$

Fig. 4.



be the initial meridian and  $OB'B$  perpendicular to it. Project the curve  $APBC$  orthogonally on the plane  $OB'B$ , then we shall get a curve  $A''P''B''C''$ . Denote the area bounded by  $A''P''B''C''A''$  by  $s_1$ . If the angle between the plane  $OP'P$

and the initial meridian be  $\theta$ , then evidently

$$s_1 = \int_0^{\pi} u \cdot r \cdot \cos \theta \cdot d\theta$$

But since  $x : H = \theta : \pi$

$$\theta = \frac{\pi x}{H},$$

we have, therefore,

$$\begin{aligned} s_1 &= \frac{r\pi}{H} \int_0^H u \cdot \cos \frac{\pi x}{H} dx \\ &= \frac{r\pi}{H} \cdot \frac{b_1 H}{2} = \frac{\pi r}{2} b_1, \end{aligned}$$

Similarly if the scale of the abscissa be so taken that the curve covers the surface of the cylinder from  $\theta = 0$  to  $\theta = p\pi$  and the area obtained by projecting it on the meridian at  $\theta = \frac{\pi}{2}$  be denoted by  $s_1$ , then

$$s_p = \frac{\rho \pi r}{2} b_p \quad (8)$$

Hence if  $S_p$  be the corresponding area for the curve at  $t=0$ , we have

$$\frac{S_p}{s_p} = \frac{B_p}{b_p}$$

and therefore

$$k = \frac{H^2}{\rho^2 \pi^2 t} \cdot \log_e \left( \frac{S_p}{s_p} \right),$$

so that if it is only required to find  $k$ , it is sufficient to determine  $S_p$  and  $s_p$  in any arbitrary unit.

I used only  $S_1$  and  $s_1$  in my reductions for the reason already given. The values of  $\log_{10} \left( \frac{S_1}{s_1} \right)$  were tabulated against  $t$ , and the ratio  $\log_{10} \left( \frac{S_1}{s_1} \right) / t$  was determined by the method of the least squares, and finally  $k$  was calculated by the equation

$$k = 2.3026 \frac{H^2}{\pi^2 t} \log_{10} \left( \frac{S_1}{s_1} \right). \quad (10)$$

§ 4. In my experiment, the diffusion vessel is made of brass (though evidently glass is preferable). Its height is 48 mm., its thickness 10 mm. and its breadth 56 mm. The spectrometer circle reads to 10 '' by verniers, and the readings of two distinct settings for the diffusion curve seldom differed by more than 20''. The angles of the prism used are

$$A = 45^\circ \quad 2' \quad 25''$$

$$B = 44^\circ \quad 55' \quad 35''$$

$$C = 90^\circ \quad 1' \quad 30''$$

The index of refraction  $N$  was measured by filling the vessel with liquids of known indices, or when vacant, and the mean of several experiments gave

$$N = 1.53175.$$

In the tables III<sub>a</sub>—III<sub>c</sub>, which relate to a set of experiments on NaCl solution,  $n_{\text{obs}}$  is the value of the index of refraction at a point  $x$  deduced from  $\theta$  by the equation (4), and  $n_{\text{cal}}$  is that value of  $n$  calculated by putting  $B_0$  and  $B_1$  or  $b_0$  and  $b_1$  obtained by harmonically analysing  $n_{\text{obs}}$  in the equation (6) or (6').  $\Delta$  is  $n_{\text{obs}} - n_{\text{cal}}$ , and shows how soon  $b_2, b_3, \dots$  become insignificantly small. In these experiments, the angle  $\alpha$  of the prism =  $45^\circ 2' 25''$ .

Table III<sub>a</sub>.

Time = 31. Jan. 14<sup>h</sup> 58<sup>m</sup>; temperature =  $10^\circ.7$  C

Spect. reading for the normal =  $329^\circ 53' 10''$ .

$x$	Spect. reading	$\theta$	$n_{\text{obs.}}$	$n_{\text{cal.}}$	$\Delta$
48	354° 11' 10"	34° 18' 0"	1.3348	1.3316	+ 0.0032
44	12 10	19 0	349	311	+ 38
39	12 10	19 0	349	334	+ 15
34	11 50	18 40	349	372	— 23
29	14 10	21 0	352	421	— 69
26	24 50	31 40	366	453	— 87
24	355 2 40	25 9 30	417	475	— 58
22	356 5 40	26 12 30	500	497	+ 3
20	357 0 20	27 7 10	569	524	+ 45
18	32 10	29 0	596	540	+ 56
16	40 50	47 40	619	560	+ 59
14	43 0	49 50	621	578	+ 43
9	44 40	51 30	623	616	+ 7
4	44 40	51 30	623	639	— 16
0	44 40	51 30	623	644	— 21

$$B_0 = 1.34749,$$

$$B_2 = +0.00207,$$

$$B_1 = +0.01693,$$

$$B_3 = -0.00453.$$



Table III<sub>b</sub>Time=1. Feb. 10<sup>h</sup> 50<sup>m</sup>; temperature=9°.8 C

Spect. reading for the normal=329° 50' 30."

$x$	Spect. reading	$\theta$	$n_{\text{obs.}}$	$n_{\text{cal.}}$	$\Delta$
48	354° 45' 10"	24° 23' 40"	1.3355	1.3351	+0.0004
44	47 20	25 50	358	355	+ 3
39	58 10	36 40	373	372	+ 1
34	355 13 50	52 20	394	400	— 6
29	41 0	25 19 30	430	435	— 5
24	356 11 50	50 20	474	474	0
19	46 20	26 24 50	514	514	0
14	357 20 50	59 20	558	550	+ 8
9	39 10	27 17 40	582	577	+ 5
4	52 30	31 0	598	594	+ 4
0	52 30	31 0	598	598	0
$b_0=1.34747,$			$b_2=+0.00021$		
$b_1=+0.01235,$			$b_3=-0.00037$		

Table III<sub>c</sub>Time=2. Feb. 13<sup>h</sup> 19<sup>m</sup>; temperature=11°.00 C

Spect. reading for the normal=330° 20' 0."

$x$	Spect. reading.	$\theta$	$n_{\text{obs.}}$	$n_{\text{cal.}}$	$\Delta$
48	355° 13' 30"	24° 53' 30"	1.3395	1.3397	-0.0002
44	15 50	55 50	398	400	— 2
39	26 0	25 6 0	412	411	+ 1
34	39 0	19 0	429	430	— 1
29	58 20	38 20	455	454	+ 1
24	356 19 40	59 40	483	481	+ 2
19	41 10	26 21 10	510	508	+ 2
14	59 50	39 50	533	533	0

9	357	14	30	54	30	552	551	+	1
4		19	50	59	50	559	563	—	4
0		20	30	27	0	560	566	—	6

$$b_0=1.34814$$

$$b_1=0.00843$$

Table III<sub>a</sub>.

Time= 3. Feb. 9<sup>h</sup> 18<sup>m</sup>; temperature=10.° 2 C.

Spect. reading for the normal=330° 20' 20"

$x$	Spect. reading	$\theta$	$n_{\text{obs.}}$	$n_{\text{cal.}}$	$\Delta$
48	355° 29' 50"	25° 9' 30"	1.3417	1.3419	—0,0002
44	31 40	11 20	419	421	— 2
39	39 0	18 40	429	429	0
34	50 50	30 30	445	443	+ 2
29	356 5 0	44 40	463	461	+ 2
24	19 30	59 10	482	481	+ 1
19	35 30	26 15 10	502	500	+ 2
14	48 10	27 50	518	518	0
9	58 40	38 20	531	531	0
4	357 3 30	43 10	538	540	— 2
0	3 50	43 30	540	542	— 2

$$b_0=1.34805$$

$$b_1=0.00614$$

Table III<sub>e</sub>.

Time=4. Feb. 10<sup>h</sup> 8<sup>m</sup>; temperature=10°.OC.

Spect. reading for the normal=330° 18' 40."

$x$	Spect. reading	$\theta$	$n_{\text{obs.}}$	$n_{\text{cal.}}$	$\Delta$
48	355° 45' 20"	25° 26' 40"	1.3440	1.3438	+0,0002
44	46 40	28 0	441	440	+ 2
39	50 10	31 30	446	445	+ 1

34		58	0		39	20	456	455	+	1
29	356	8	10		49	30	469	467	+	2
24		18	30		59	50	481	481		0
19		29	20	26	10	40	497	495	+	2
14		38	50		20	10	509	508	+	1
9		46	10		27	30	518	518		0
4		50	10		31	30	523	524	—	1
0		50	10		31	30	523	525	—	2

$$b_0 = 1.34814$$

$$b_1 = 0.00407.$$

The curves a-e in plate I, are the  $n$ - $x$  curves with  $x$  as the ordinate and  $n$  as the abscissa ; and those in plate II, are the curves obtained by projecting them supposed to be wrapped round a cylinder on the meridian plate perpendicular to the initial meridian, and are used in calculating  $B_1$  and  $b_1$ . Table IV and the line  $a$  in plate V show the relation between  $t$  and  $\log_{10}\left(\frac{B_1}{b_1}\right)$ . They show how nearly  $\log_{10} \times \left(\frac{B_1}{b_1}\right)$  is proportional to  $t$ , as is required by Fick's law, and that fact may be looked upon as a proof that at least in NaCl,  $k$  is independent of the concentration.

Table IV.

Time.	Temp.	$t$ (day)	$B$ , and $b$ ,	$\log_{10} \left( \frac{B_1}{b_1} \right)$
31. Jan. 14 <sup>h</sup> 58 <sup>m</sup>	10°.7C	0.000	+0.01693	0.0000
1 Feb. 10 50	9.8	0.828	1235	0.1370
2 „ 13 19	11.0	1.931	843	0.3029
3 „ 9 18	10.2	2.763	614	0.4405
4 „ 10 8	10.0	3.798	407	0.5882

$$k = 0.841 \left( \frac{\text{cm}^2}{\text{day}} \right) = 9.73 \times 10^{-6} \left( \frac{\text{cm}^2}{\text{sec}} \right)$$

$$\text{Mean temp} = 10°.3 \text{ C}$$

§5 In the experiment for  $\text{Zn SO}_4$ , the angle  $\alpha$  of the prism =  $44^\circ 55' 35''$ . The results are given in Tables Va—Vf. As  $n$  is not a linear function of  $u$ , we have to reduce  $n$  to  $u$  in this case. In the following tables, the numbers in the column  $u$  are the number of grammes of  $\text{Zn SO}_4$  in 100 grammes of water. I have dispensed with calculating  $B_0, B_1, \dots$ , and the areas  $S_1$  and  $s_1$  in an arbitrary unit were determined only, because the fact that the phenomena of diffusion is fairly well represented by the equation (5), was made clear by the experiments on  $\text{NaCl}$ , and because in the determination of  $k$ , a knowledge of  $S_1$  and  $s_1$  is sufficient.

Table V<sub>a</sub>.

Time = 13. Feb. 16<sup>h</sup> 43<sup>m</sup>; temperature =  $12^\circ.00$

Spect. reading for the normal =  $358^\circ 54' 20''$

$x$	Spect. reading	$\theta$	$n$	$u$
48 <sup>mm</sup>	23° 24' 10"	24° 29' 50"	1.3348	0.98
43	24 10	29 50	348	0.98
38	24 20	30 0	349	0.98
33	26 50	32 30	352	1.24
31	35 0	40 40	363	2.22
29	24 1 50	25 7 30	399	5.24
27	58 10	26 3 50	474	14.09
25	26 34 30	27 40 10	596	30.42
23	28 0 30	29 6 10	700	48.22
21	28 10	33 50	733	53.04
18	32 40	38 20	738	56.20
13	32 30	38 10	738	56.20
8	32 30	38 10	738	56.20
3	32 30	38 10	738	56.20
0	32 30	38 10	738	56.20

$S_1 = 1073.5$

Table V<sub>b</sub>.Time=14. Feb. 13<sup>h</sup> 29<sup>m</sup>; temperature=11°. 2 C.

Spect. reading for the normal=358° 55' 40".

$x$	Spect. reading			$\theta$			$n$	$u$
48 <sup>mm</sup>	23°	28'	10"	24°	32'	30"	1.3352	1.24
43		28	30		32	50	352	1.24
38		40	50		45	10	369	2.76
33	24	12	0	25	16	20	411	6.82
28	25	18	20	26	22	40	498	16.73
23	26	50	0	27	54	20	613	33.20
18	28	0	10	29	4	30	698	47.38
13		28	20		32	40	731	54.70
8		35	10		39	30	740	56.58
3		35	30		39	50	740	56.58
0		35	30		39	50	740	56.58

$s_1=1006.0$

Table V<sub>c</sub>.Time=15. Feb. 10<sup>h</sup> 25<sup>m</sup>; temperature=10°. 3 C.

Spect. reading for the normal=358° 54' 50".

$x$	Spect. reading			$\theta$			$n$	$u$
48 <sup>mm</sup>	23°	35'	10"	24°	40'	20"	1.3363	2.22
43		40	0		45	10	369	2.75
38		56	40	25	1	50	390	4.58
33	24	30	40		35	50	437	9.50
28	25	27	10	26	32	20	511	18.21
23	26	36	0	27	41	10	597	28.76
18	27	32	20	28	37	30	666	42.23
13	28	12	20	29	17	30	713	50.93
8		27	50		33	0	731	54.68

3	33	20	38	30	739	56.38
0	33	20	38	30	739	56.38

$s_1=920.0$

Table  $V_a$ .

Time=18. Feb. 9<sup>h</sup> 26<sup>m</sup>; temperature=11.°OC.

Spect. reading for the normal=358° 54' 50."

$x$	Spect. reading	$\theta$	$n$	$u$
48	24° 15' 20"	25° 20' 30"	1.3416	7.29
43	19 10	24 20	422	7.74
38	35 30	40 40	443	10.17
33	25 3 10	26 8 20	479	14.88
28	39 50	45 0	526	20.12
23	26 21 40	27 26 50	579	28.22
18	27 2 20	28 7 30	629	35.88
13	36 10	41 20	670	42.92
8	28 0 50	29 6 0	700	47.46
3	12 30	17 40	714	51.15
0	12 30	17 40	714	51.15

$s_1=692.0$

Table  $V_e$ .

Time=20. Feb. 14<sup>h</sup> 21<sup>m</sup>; temperature=10° 7 C.

Spect. reading for the normal=358° 55' 50".

$x$	Spect. reading	$\theta$	$n$	$u$
48	24° 37' 50"	25° 42' 0"	1.3436	9.37
43	43 0	47 10	452	11.18
38	54 30	58 40	467	13.48
33	25 17 30	26 21 40	496	16.62
28	45 50	50 0	532	20.89

23	26	18	10	27	22	20	573	27.64
18		51	20		55	30	614	33.30
13	27	19	50	28	24	0	650	39.48
8		41	50		46	0	676	43.95
3		51	50		56	0	688	47.25
0		51	50		56	0	688	47.25

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$s_1=577.5$

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Table V<sub>r</sub>.Time=21. Feb. 16<sup>h</sup> 33<sup>m</sup>; temperature=10°.7 C.

Spect. reading for the normal=358° 55' 50."

$x$	Spect. reading			$\theta$			$n$	$n$
48	24°	48'	10"	25°	52'	20"	1.3459	12.23
43		50	20		54	30	462	12.70
38	25	3	50	26	8	0	479	14.88
33		22	40		26	50	503	17.34
28		49	10		53	20	537	21.70
23	26	15	50	27	20	0	571	27.11
18		46	30		50	40	608	32.26
13	27	12	20	28	16	30	640	37.77
8		33	30		37	40	666	42.20
3		42	40		46	50	677	44.14
0		42	40		46	50	677	44.14

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$s_1=509.5$

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Figures a-f in plate III. are  $n$ - $x$  curves, and those in plate IV are the curves used in determining  $S_1$  and  $s_1$ . Table VI. and the line b in plate V show the relation between  $t$  and  $\log_{10} \left( \frac{S_1}{s_1} \right)$ .

Table VI.

Time.				Temp.	t (day)	$\log_{10} \frac{S_1}{s_1}$	$S_1$ and $s_1$
13.	Feb.	16 <sup>h</sup>	43 <sup>m</sup>	12.°C	0.600	0.0000	1073.5
14	„	13	29	11.2	0.865	282	1006.0
15	„	10	25	10.3	1.720	670	920.0
18	„	9	26	11.0	4.697	1907	692.0
20	„	14	21	10.7	6.901	2693	577.5
21	„	19	33	10.7	7.985	3237	509.5

$$k = 0.2145 \left( \frac{\text{cm}^2}{\text{day}} \right) = 2.483 \times 10^{-6} \left( \frac{\text{cm}^2}{\text{sec}} \right).$$

Mean temp. = 11°.0 C.

§ 6 I conclude from the preceding experiments that so far as NaCl and  $\text{ZnSO}_4$  are concerned,  $k$  is independent of the concentration, and Fick's law is satisfied fairly well by them. As to the numerical values of  $k$ , the results of several experimenters do not agree with one another. Table VII is formed by reducing the experiments of Graham, Scheffer and Schuhmeister under the supposition that  $k$  is a function of temperature only.

Table VII.

Substance	Temperature	$k \left( \frac{\text{cm}^2}{\text{day}} \right)$	Observer
NaCl	10.° C	0.95	Graham
„	„	0.86	Schuhmeister
„	„	0.87	Scheffer
„	10.3	0.84	Nakamura
$\text{ZnSO}_4$	10.0	0.20	Schuhmeister
„	9.5	0.18	Weber
„	11.0	0.21	Nakamura

§ 7. If  $k$  be taken as a linear function of  $u$  as was supposed by



Wiedeburg and Wiener, and be put equal to  $\alpha + \beta u$ , then the differential equation (3) gives at once,

$$\frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial x^2} + \frac{\beta}{2} \frac{\partial^2 (u^2)}{\partial x^2}.$$

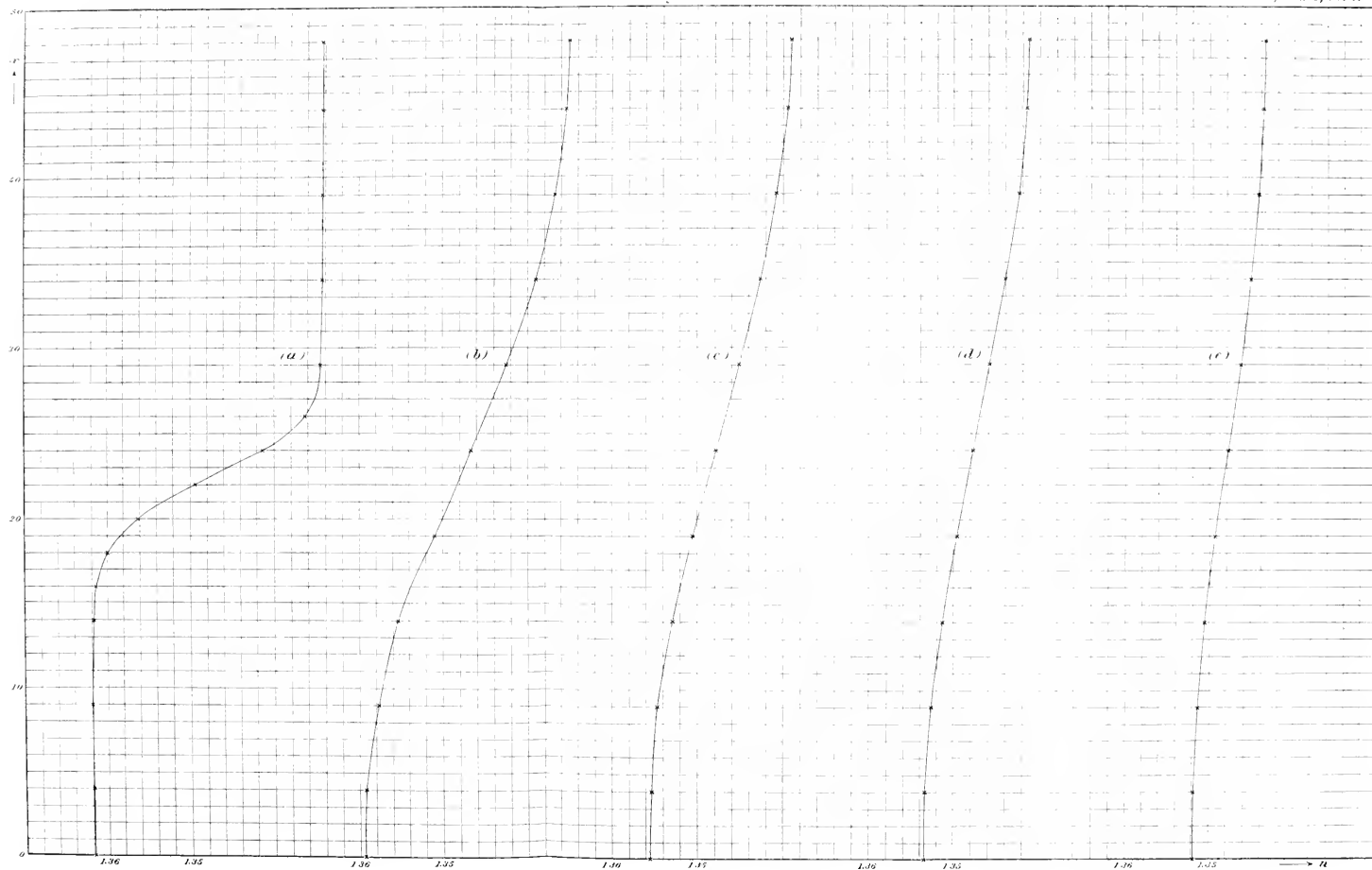
As  $u$ - $x$  curves for various values of  $t$  are known, we can determine  $\frac{\partial u}{\partial t}$  and  $\frac{\partial^2 u}{\partial x^2}$  graphically for given values of  $x$  and  $t$ , and by plotting  $u^2$  against  $x$ , we can also determine  $\frac{\partial^2 (u^2)}{\partial x^2}$ , and thus calculate  $\alpha$  and  $\beta$ . But as this method is lacking in accuracy, I did not undertake the task.

March 7, 1903.

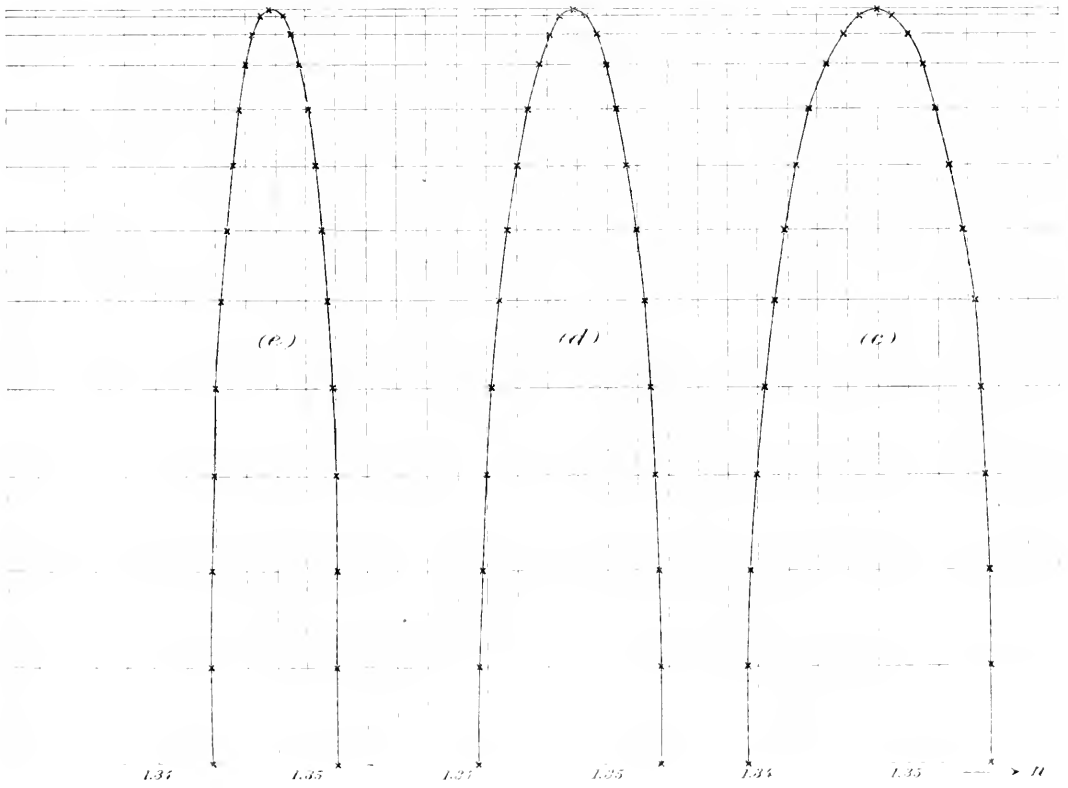
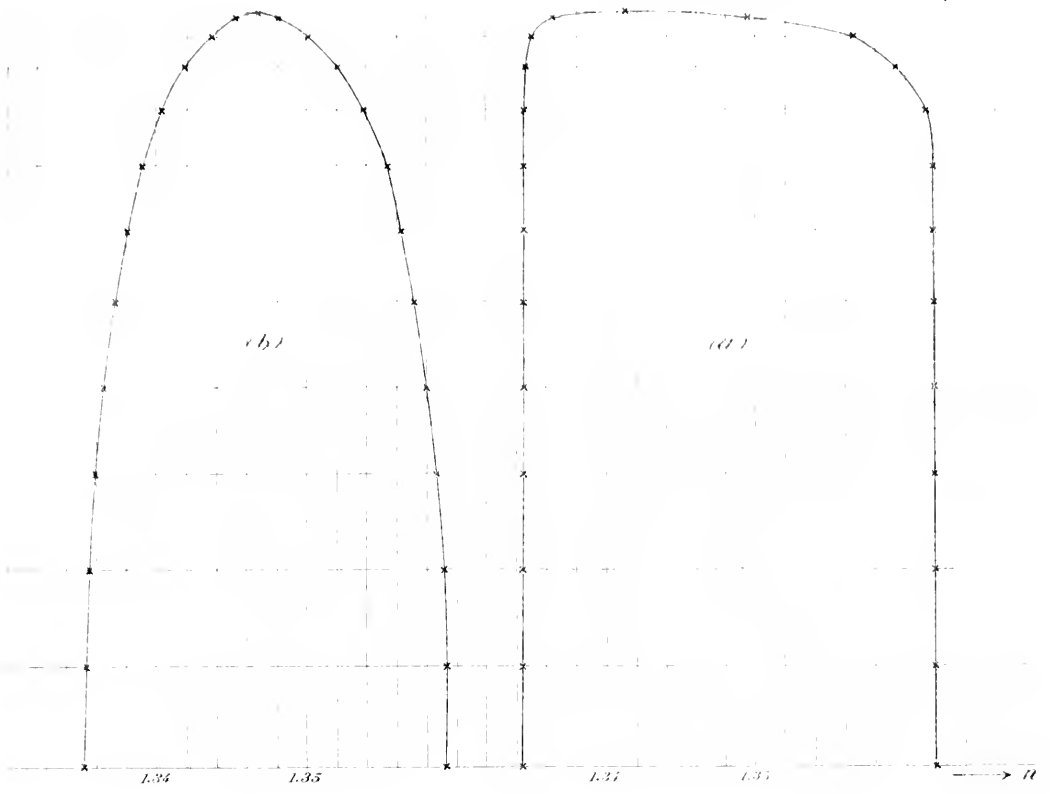
Physical Institute, Imp. Univ. of Tokyō.



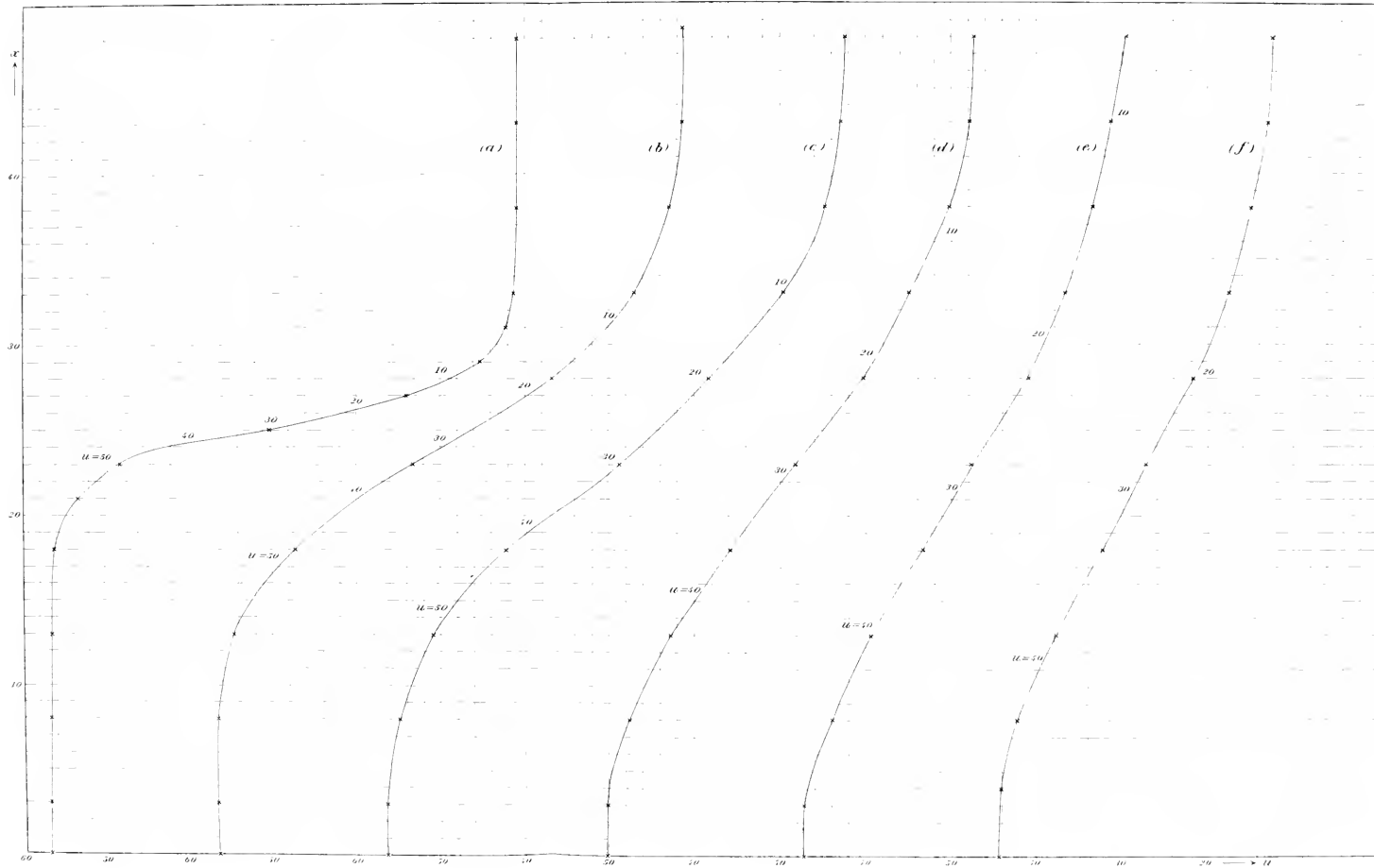






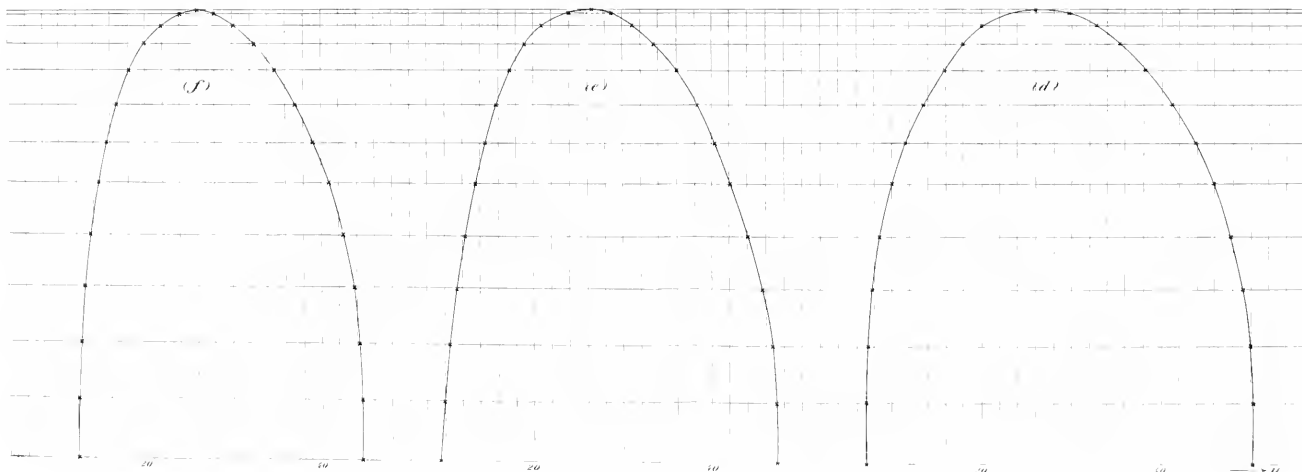
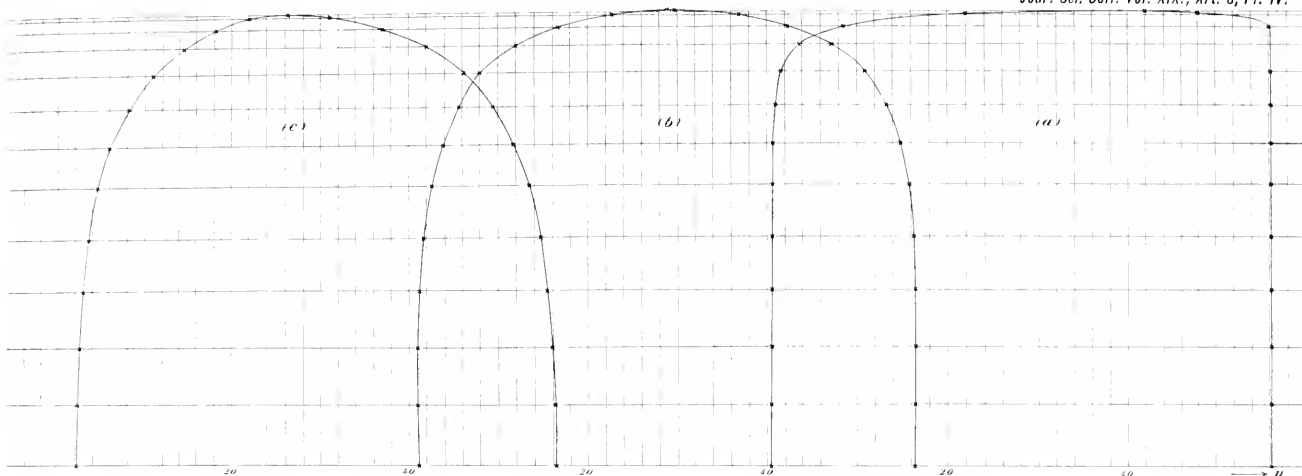




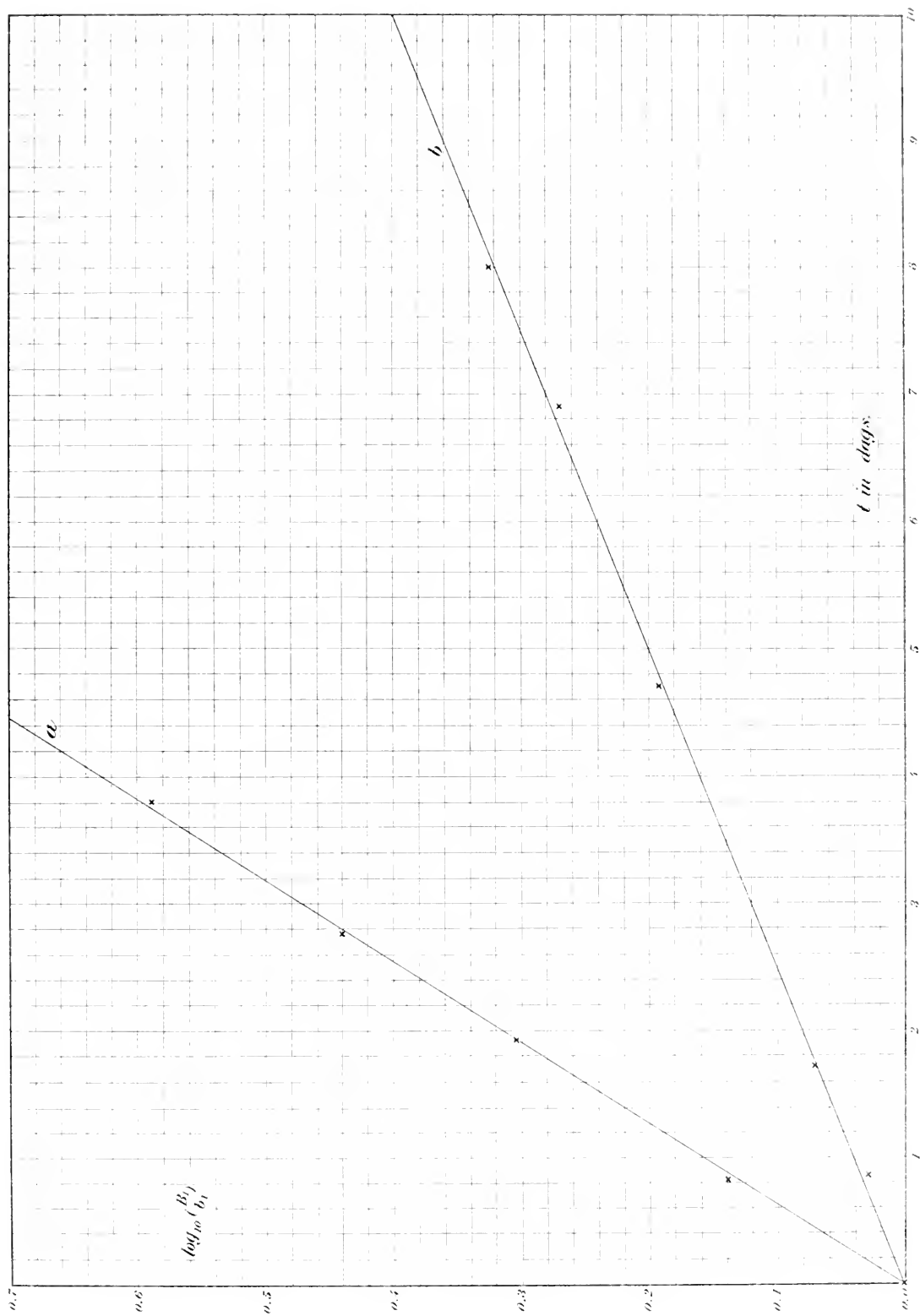














## Effect of Temperature on the Magnetization of Steels, Nickel and Cobalt, measured magnetometrically.

By

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and

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(With two plates).

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§ 1. The importance of studying the effect of temperature on the magnetization of ferromagnetic bodies has long been recognised by physicists on account of its significant bearing on the molecular theory of magnetism. As early as 1825, KUPFFER investigated the effect of heating upon the temporary magnetism of iron; later we find the names of FARADAY, WIEDEMANN, GAUGAIN, ROWLAND, BAUR, TROWBRIDGE, TOMLINSON, and LEDEBOER<sup>1)</sup> in the list of those who have investigated the effect of heating on magnetization.

The numerous experiments on the magnetization of ferromagnetic substances at different temperatures were for the most

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1) WIEDEMANN's *Elektricität*, III. 1896; EWING, *Magnetic Induction*; DU BOIS, *Art. Propriétés magnetiques de la matière pondérable, Rapports présentés au Congrès international de Physique*, Paris, 1900.

part qualitative until the decided advance in quantitative determination made by the researches of HOPKINSON<sup>1)</sup> and CURIE.<sup>2)</sup> Although the former used the ballistic method and his magnetizing field was not strong, yet he did not fail to bring to light the principal features of the change in magnetization near the critical temperature. CURIE utilized the mechanical force brought into play, when a ferromagnetic body is placed in a heterogeneous field. The magnetization could hardly have been uniform throughout, but the method was well adopted for heating the substance beyond the melting point and for examining its magnetic quality in fields scarcely attainable by means of a magnetizing coil. It would be superfluous to enter into a discussion of the advantages and disadvantages of the methods and arrangements of HOPKINSON and CURIE, suffice it to remark, that the magnetometric method is after all the best suited for the investigation of the change of magnetization near the critical temperature. We are however beset with difficulties in arranging the magnetizing coil and the heating apparatus within a small compass, so as to insure at the same time, the uniformity of the field and of the temperatures.

The present paper<sup>3)</sup> gives a description of experiments made more than two years ago, for the purpose of studying the temperature effect on the magnetization of iron, various kinds of steels, nickel, and cobalt ovoids. The measurement of the intensity of magnetization was made by means of a magnetometer, and the heating was effected by gasflames, instead of following the usual method of raising the temperature by an electric current.

§ 2. *Method of Experiment.*—The method adopted in the

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1) HOPKINSON, *Phil. Trans.* for 1889, p. 443.

2) CURIE, *Ann. de Chim. et de Phys.* **5**, 289, 1895.

3) An abstract of the paper is given in Reports of the Tōkyō Mathematico-physical Society for September, 1902.

present experiment permits examining the magnetizations at different temperatures up to about  $1200^{\circ}\text{C}.$ , either by keeping the external magnetizing field constant, or in varying fields, by means of a simple magnetometer.

A magnetizing coil (length 40 cm., wound in 10 layers;  $4\pi n = 394.4$  resistance = 1.51 ohm.) was waterjacketed and the inner face of the core protected by thick asbestos paper. A burner (Fig. 1) consisting of three branching copper tubes, coated with asbestos, was placed in the coil and fed with gas and air blast. Fine jets of flame (90 in all) issued horizontally, and played on the outer cover of the ferromagnetic ovoid. All the ovoids were 1 cm. thick and 20 cm. long, with the demagnetizing factor  $N = 0.0836$ . They were placed between the projecting knobs in the burner as shown in the figure. A platinum-rhodium and platinum junction was brought in contact with the ovoid at its thickest part, while the rest was insulated with asbestos paper.

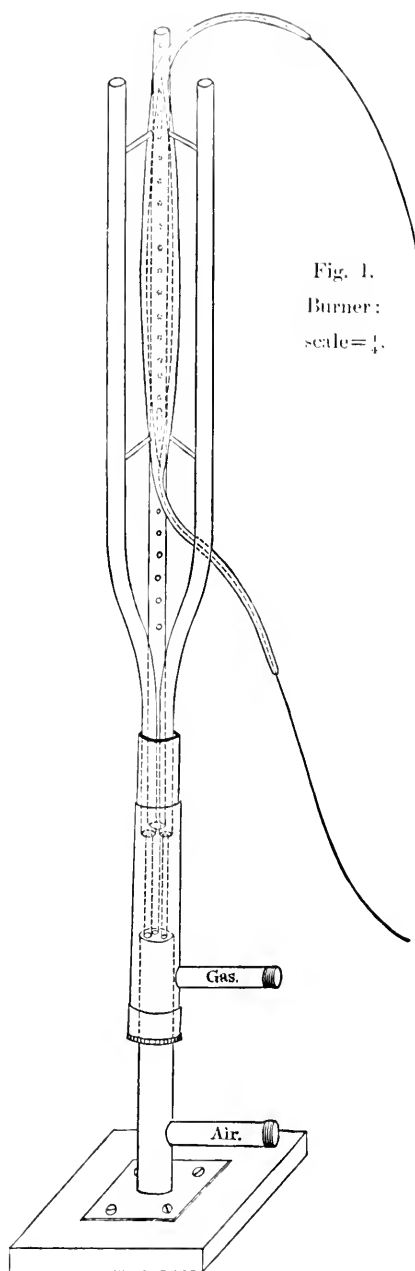


Fig. 1.  
Burner;  
scale =  $\frac{1}{4}$ .

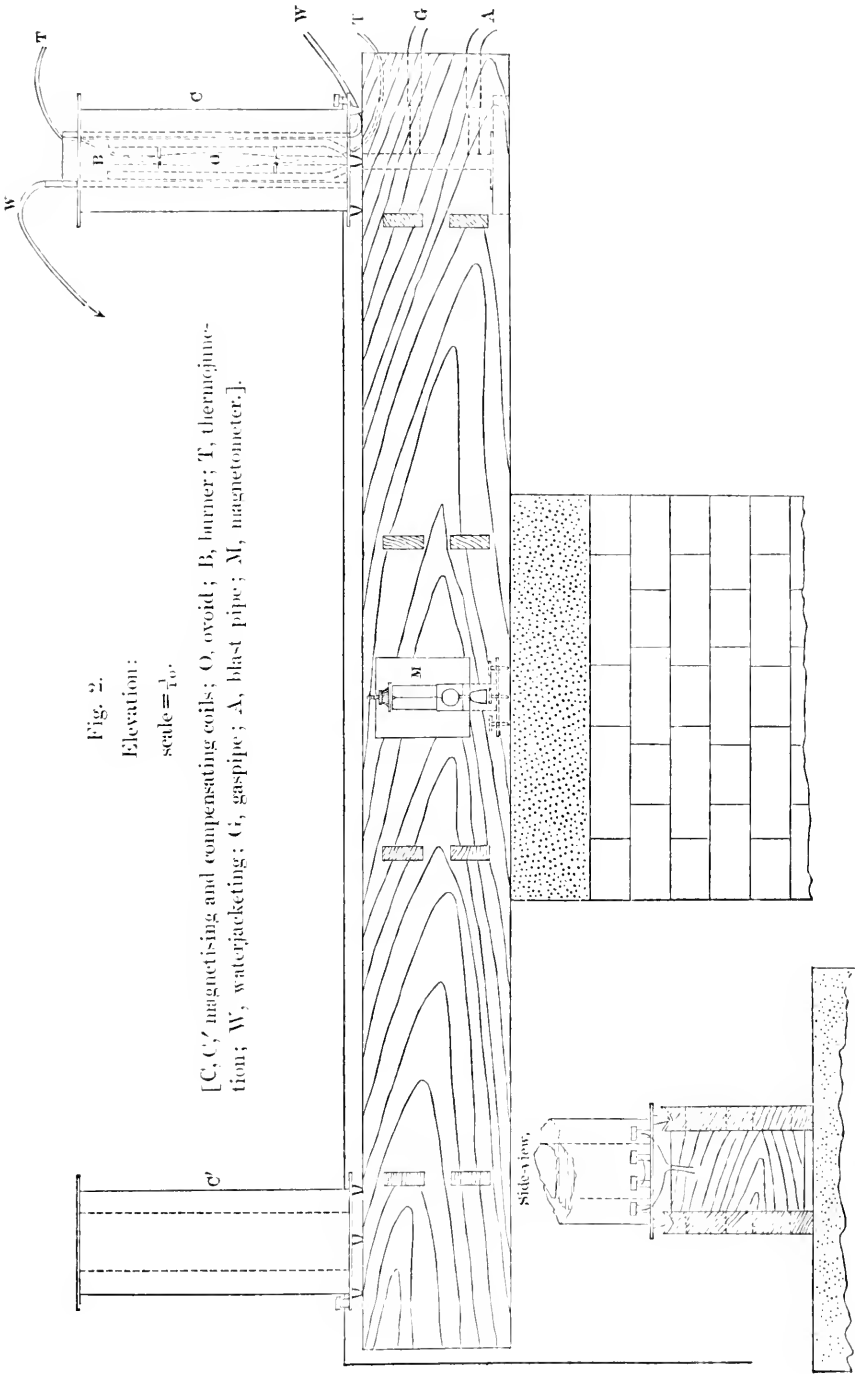
The ovoid, together with the element leaving its extremities outside the coil, was thickly coated with asbestos paper, so that the temperature variation of the ovoid was very small even at  $1000^{\circ}\text{C}$ . The ovoid was placed vertically in the middle of the coil, as shown by the dotted lines in Fig. 1 and Fig. 2. The vertical component of the terrestrial magnetic field was compensated by a coil wound outside the magnetizing coil.

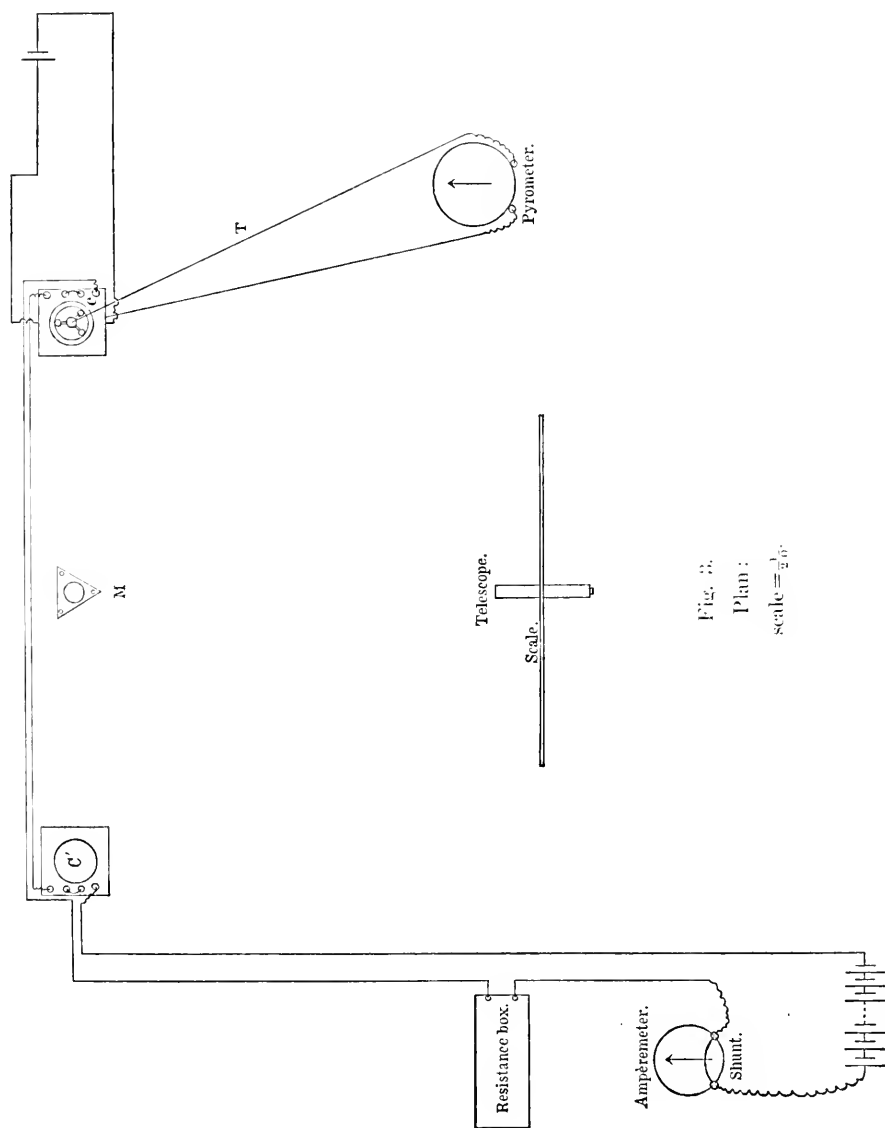
A magnetometer with a small bell-shaped magnet suspended by a fine quartz fibre was placed in such a position that the effect of a small vertical displacement of the ovoid was quite negligible. This was effected by placing the magnetometer in such a position that the line joining the centre of the ovoid with the magnetometer magnet was inclined at an angle, whose tangent  $=\frac{1}{2}$  with the horizontal line, in the vertical plane containing the axis of the coil and the magnetometer. On the other side of the magnetometer symmetrical with the magnetizing coil, was placed another coil of the same strength, to compensate the effect of the coil on the magnetometer. In order to ensure the smallest possible displacement of the coils so as to get accurate compensation, they were placed on a wooden bench with V-shaped grooves lined with brass plates, on which the levelling screws of the coils rested. These coils were fed by accumulators. The current was measured by a Siemens and Halske amperemeter.

The temperature of the ovoid was measured by a thermoelectric junction with a D'Arsonval galvanometer in series, and the constant of the pyrometer was tested by means of a mercury thermometer to about  $300^{\circ}$  and by the melting point of sodium chloride at  $780^{\circ}$ .

The annexed figures show the arrangement in plan and in elevation.







In order to avoid external disturbances, the observations were made during the night. The scale readings could be easily read to  $\frac{1}{10}$  of a mm., which corresponded to ca. 4.6 C.G.S. in the intensity of magnetization, but it was impossible to read the D'Arsonval galvanometer more accurately than to within a few degrees of the centigrade scale, when temperature was above  $700^{\circ}$ , although the fluctuations were generally slow.

It may here be mentioned that a magnetometric study on the effect of temperature on the magnetization of basalt has been made recently by ALLAN,<sup>1)</sup> although the heating was done with electricity.

§ 3. As the results obtained with iron ovoids do not differ particularly from those already obtained by HOPKINSON<sup>2)</sup>, CURIE<sup>3)</sup> LYDALL and POCKLINGTON,<sup>4)</sup> MORRIS,<sup>5)</sup> and WILLS,<sup>6)</sup> we shall describe only our experiments with steels, nickel and cobalt.

*Steels.* Ordinary steel behaves qualitatively like iron, with the only difference that the transformation takes place at a higher temperature. Up to about  $500^{\circ}$ , the diminution of magnetization due to temperature rise is generally insignificant, but with increased temperatures the rate of diminution gradually increases till it approaches the critical temperature, which lies very close to  $820^{\circ}$ .

In cast steel, the same course as for ordinary steel is repeated at a somewhat higher temperature. The critical temperature of the specimen which we experimented with, was about  $920^{\circ}$ , being about  $100^{\circ}$  higher than that for ordinary steel.

1) ALLAN, *Phil. Mag.* Jan. 1904, p. 45.

2) HOPKINSON, *loc. cit.*

3) CURIE, *loc. cit.*

4) LYDALL and POCKLINGTON, *Proc. R. S.*, **52**, 213, 1892.

5) MORRIS, *Phil. Mag.* Sept. 1897, p. 229-230.

6) WILLS, *Phil. Mag.* July 1900, p. 1-43.

Tungsten steel behaves like ordinary steel, the only difference being that the critical temperature is about  $900^{\circ}$ .

*Nickel.* The susceptibility of nickel decreases with rise of temperature; which is more marked as we approach the transition stage; the magnetization soon reaches saturation, so that its increase after  $H=100$  is extremely small. The specimen was nearly pure, and indicated evanescence of magnetization at about  $500^{\circ}$ . It must, however, be borne in mind that these temperatures in all the ferromagnetics depend on the field strength as well as on the history of the previous heating or cooling, as will be shown later in the experiments in fields of constant strength.

*Cobalt.* Of all the ferromagnetic substances which we examined, cobalt alone was characterized by several remarkable changes by magnetization due to the raising of its temperature, although most of the effects were equally participated in by other ferromagnetics.

The magnetization at ordinary temperatures is generally weak in low fields, but gradually increases at a steady rate, so that even in a field of 500 units, the magnetization can not be said to be in a saturated condition. With increase of temperature, the 'wendepunkt' gradually recedes towards low fields, and the magnetization on the whole increases in all fields. At about  $500^{\circ}$ , the increase reaches its maximum, and is about twice as great as at ordinary temperatures. Thus the effect of temperature is singularly large in cobalt. With further increase of temperature, the magnetization in low fields increases while that in high fields decreases, and the nature of the change wrought by raising the temperature of the metal resembles that in iron and nickel. The curves of magnetization at high temperatures gradually become less steep in high fields, while those at low temperatures show

the opposite tendency. Retaining these features up to about  $900^{\circ}$ , the rate of the fall of magnetization with a still further increase of temperature becomes very great, and the curve of magnetization at  $1140^{\circ}$  lies flat along the axis of null magnetization.

One of us had already shown that cast cobalt undergoes remarkable changes by annealing both as regards magnetization and magnetostriction. The specimen here experimented upon was an annealed ovoid; it showed that successive heatings produce small changes, so that after cooling the metal the curve of magnetization is slightly displaced as shown in the figure.

The following table contains the results of observations.



rather slowly, and we can follow it by the magnetometric method, while the ballistic method does not allow us to trace the change in its successive phases.

*Ordinary Steel.* The curve (Fig. 9, Pl. II.) shows the slight, increase of magnetization with temperature rise. The fall of magnetization takes place very rapidly after passing  $700^{\circ}$ , until it finally vanishes at about  $830^{\circ}$ . A remarkable feature is revealed on cooling. The return curve does not retrace the heating curve, but the metal must be cooled about  $40^{\circ}$  below the critical temperature, before the magnetization, which had disappeared in the heating, again makes its appearance. The increase of magnetization in cooling takes place slowly after reappearance, but eventually the increase becomes very rapid, and attains such values that the curve crosses the heating curve, and lies above it when the temperature is below  $650^{\circ}$ .

Further cooling results in a slight increase of magnetization. The curve representing the variation of magnetization with temperature is generally very smooth.

*Tungsten steel.* The change in tungsten steel is of a complex character. Before reaching the temperature of the sudden drop in magnetization on heating and after passing that of the sudden rise on cooling, we notice at least five corrugations in the curves of magnetization in a constant field. In an experiment in  $H' = 39.8$ , the corrugations lie at about  $300^{\circ}$ ,  $430^{\circ}$ ,  $510^{\circ}$ ,  $580^{\circ}$  and  $730^{\circ}$ . The curve drops abruptly between the temperatures  $830^{\circ}$  and  $880^{\circ}$ , showing evanescence of magnetization at about  $910^{\circ}$ . The retardation in the reappearance of magnetization on cooling is very remarkable. When once the magnetization disappears it can not be recovered until the temperature is lowered by about  $240^{\circ}$ , so that it reappears at about  $570^{\circ}$ , indicating a sudden

increase between  $630^{\circ}$  and  $620^{\circ}$ . The increase, however, goes on slowly when the metal is cooled below  $600^{\circ}$ , and the curve displays singular trends, at temperatures nearly coinciding with those above mentioned. The magnetization below  $380^{\circ}$  becomes greater than that on the heating course, so that on reaching ordinary temperature, the difference between the final and initial intensities of magnetization amounts to one-third of the total intensity. In experiments in stronger fields ( $\mathfrak{H}'=118$ ) the same characteristics are shared by the heating and cooling curves as shown in Fig. 10, Pl. II. The corrugations are made more conspicuous and lie at somewhat higher temperatures.

*Nickel.* The critical temperature of this metal lies far below that of iron and cobalt, and the heating and cooling curves assume smooth courses. The specimen tested was of nearly pure nickel; the critical temperature for  $\mathfrak{H}'=39$  being about  $500^{\circ}$ ; it rose to  $580^{\circ}$  for  $\mathfrak{H}'=177$ , showing that the said temperature increases with the field strength. On cooling, we notice that the magnetization begins to recover at temperatures about  $100^{\circ}$  lower than that at which it vanishes on heating, just as in iron and steel. The difference in the magnetization after cooling down to ordinary temperature is tolerably large in moderate fields, but becomes smaller as the field strength is increased. An inspection of the curve in Fig. 11, Pl. II. will make these points clear.

*Cobalt.* The general character of the curve of magnetization plotted against temperature is the same as for other ferromagnetic bodies, but as already noticed, the variation in the magnetization of the metal surpasses all other substances thus far examined. This remarkable difference can be easily traced in the curves, of which three are given in Fig. 12, Pl. II. e.g.  $\mathfrak{H}'=39.3$ ,  $97.1$ , and  $186.7$ .

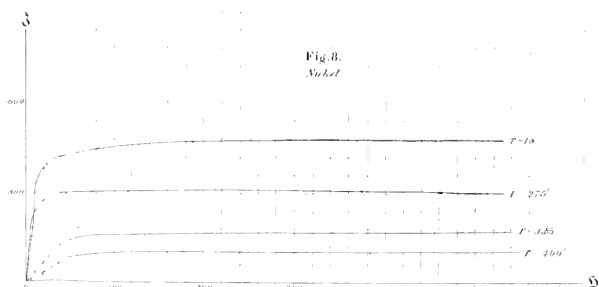
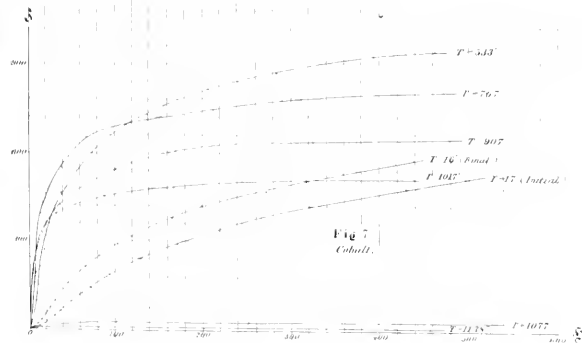
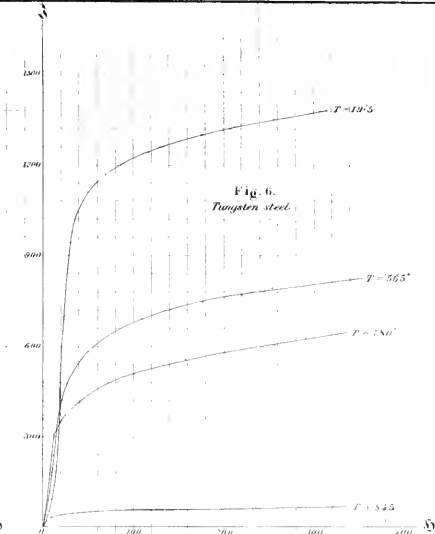
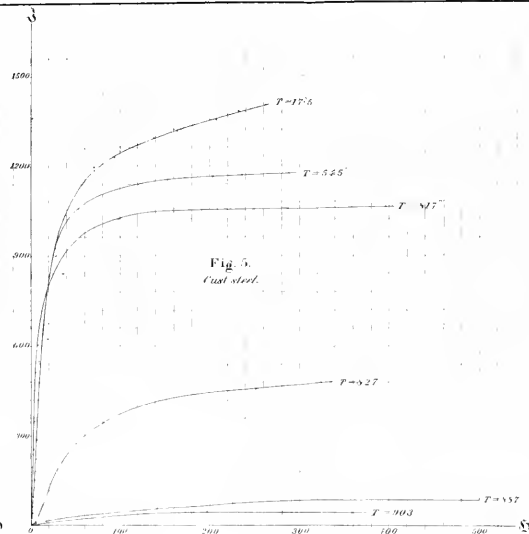
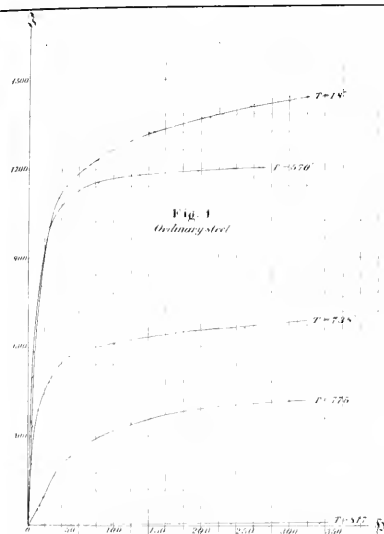


In the first place, the increase in the magnetization at  $500^{\circ}$  is nearly double the intensity at ordinary temperatures. The maximum intensity at about  $500^{\circ}$  is highly characteristic of this metal, for the decrease in the intensity takes place quite steeply as the temperature is further increased. The place of sudden decrease is carried to higher temperatures as the magnetizing forces become stronger. The cooling curve cuts the heating curve and reaches the maximum at about  $360^{\circ}$ , which is about  $140^{\circ}$  lower than that for heating. The change of magnetization either on cooling or on heating wears a rather irregular aspect, of which it is not easy to give a simple description, but the inspection of the curves will reveal the complicated nature of the change.

§ 5. *Recalescence of Tungsten steel.* The curious behaviour of tungsten steel on cooling after heating seemed at first sight to have an intimate connection with recalescence; it can be easily observed in the case of a rod of this metal. Upon heating it with the burner described above to about  $800^{\circ}$ , and then exposing it to the air, and observing the dazzling metal in the dark, we first notice a shade of dusky hue at both extremities; this gradually spreads upwards and downwards, just as dilute ink soaks into a red blotting paper. The dark portions gradually spread toward the middle of the rod, but with the lapse of time, the ends begin again to brighten. The colour now somewhat resembles that of the setting sun just emerging from a thick cloud; that part of the rod, which a few minutes before was scarcely visible, becomes tinged with red, and the clouds recede towards the middle, where they meet and disappear. The somber red thus prevails throughout the reheated rod, till it fades to a faint glimmer and disappears in complete darkness.

To ascertain the temperature at which this singular phenomenon takes place, a small hole was bored axially through a tungsten steel cylinder, into which the thermojunction could be introduced. Heating the cylinder to  $900^{\circ}$  and then leaving exposed to the air (at  $21^{\circ}$ ), the temperature of the metal during the cooling process was observed with the time; Fig. 13, Pl. II. At  $660^{\circ}$  there was an increase of temperature for a few minutes, and then a gradual decrease. This point is marked by a conspicuous prominence in the curve of cooling. At somewhat lower temperatures, we notice slight corrugations in the temperature curve, which may have some connection with similar features presented by magnetization. The approximate coincidence of the temperature of recalescence with that of steep ascent in magnetization leads us to the conclusion that they are both due to the establishment of a certain molecular arrangement at that temperature. Whether the temperature at which recalescence sets in depends on the magnetizing force, which evidently affects the cooling curve of magnetization, is a question still to be solved.







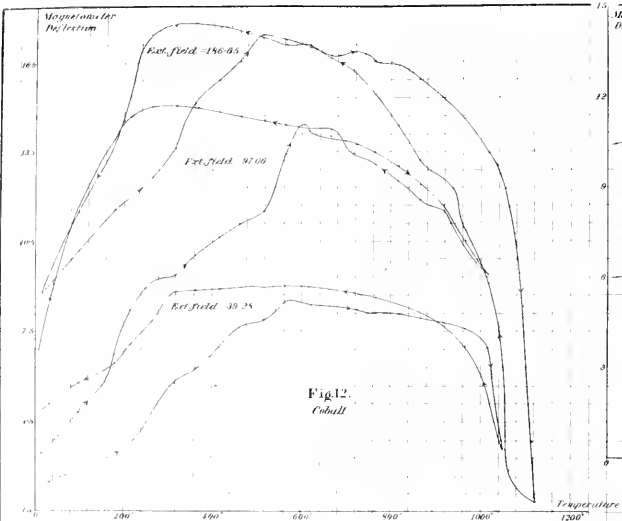


Fig. 12.  
Cobalt

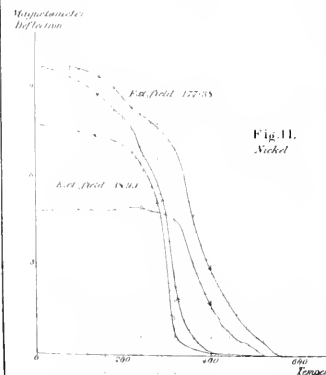


Fig. 11.  
Nickel

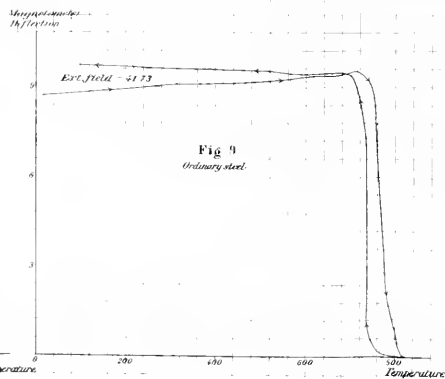


Fig. 9.  
Ordinary steel

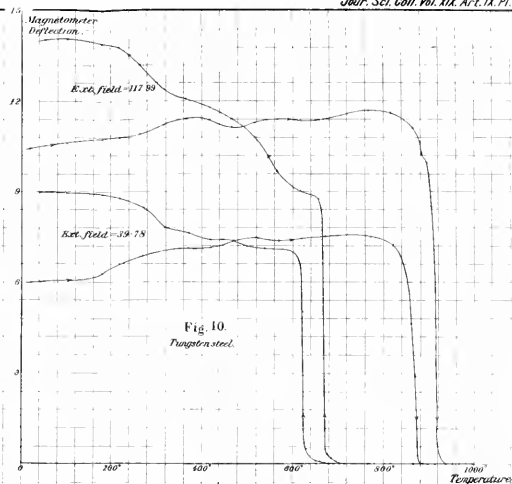


Fig. 10.  
Tungsten steel

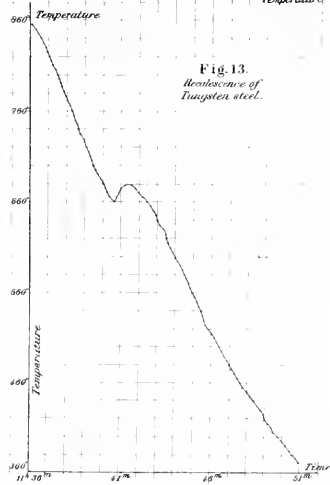


Fig. 13.  
Annealing curve of  
Tungsten steel.



## Change of Length of Ferromagnetic Substances under High and Low Temperatures by Magnetization.

By

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AND

S. SHIMIZU, *Rigakushi*.

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*With Plates I—III.*

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The interesting experiments of Hopkinson on magnetization at high temperatures promise us some important results in the magnetic change of length at such temperatures. On account, however, of the experimental difficulties, this interesting subject has as yet scarcely been investigated. Barrett\* was the first to touch the subject; with a rise of temperature of about 50°C, he observed no effect on the magnetic change of length in iron and cobalt; but in nickel, the contraction was reduced to about two-thirds of its ordinary value. A few years ago, one of us† studied the same effect in iron, tungsten steel, and nickel at temperatures ranging from 18°C to 100°C. In weak fields, the magnetic elongation of iron was slightly diminished by heating; but in strong fields, it was increased. In tungsten steel, the elongation was always diminished; in nickel, the contraction was considerably reduced except in weak fields, in which a minute increase of contraction was sometimes observed.

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\* Barrett, Phil. Mag. [4] **47**, 51, 1874; Nature **26**, 515, 586, 1882; Beibl. **7**, 201.

† K. Honda, Jour. Sc. Coll. XIII, 83, 1900.

In these experiments, the range of temperatures was very limited, so that the remarkable effect of high temperatures was not observed. In the present case, the experiments were pushed beyond the critical temperature of iron; in addition to this, the change of length in liquid air was also examined.

### § 1. APPARATUS.

The apparatus for measuring the change of length by magnetization at high and low temperatures was substantially the same as that used for the study of the effect of tension on the magnetic change of length.\* Repeated experiments showed that this arrangement gave very consistent results, but that it was rather preferable to flatten the surface of the vertically suspended wire in contact with the rotating cylinder. To diminish the effect of tension on the magnetic change of length as well as the yielding at high temperatures due to tension, thick rods about 1 cm in diameter and 21 cm in length were employed. In the experiments at high temperatures, the suspended weight was generally 1 or 2 Kilograms; its effects were consequently almost insensible. To the upper end of the ferromagnetic rod, a copper rod about 1 cm thick and 25 cm long was jointed by means of a copper screw, and then brazed. The lower end of the rod was likewise attached to a similar copper rod about 20 cm long. The screwed part in each end of the ferromagnetic rod was 1.5 mm. This connected system hung vertically from a stout support by means of a brass stand with three levelling screws. The support on which the tripod stand rested, was provided with a brass plate with a hole-slot-plane arrangement. The free end of the bar was connected with a copper wire about 1.5 mm thick

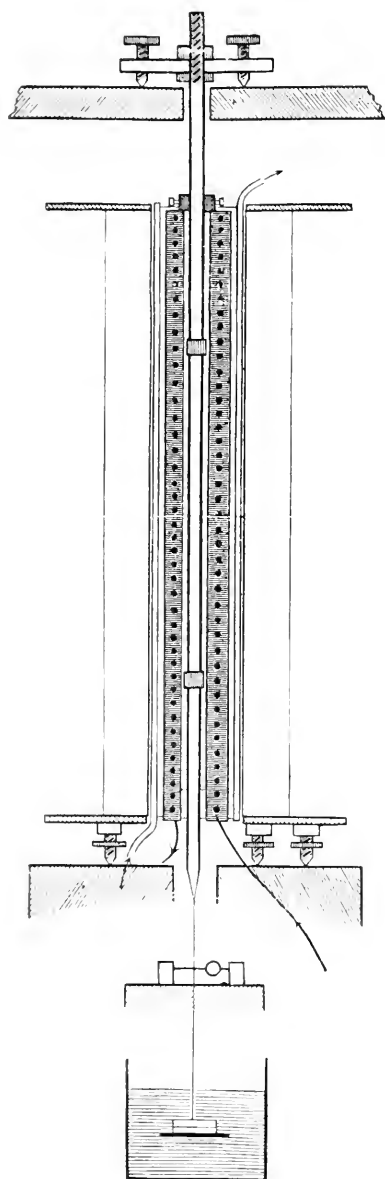
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\* K. Honda and S. Shimizu, Jour. Sc. Coll. XVI, Art. 9, 1902; Phil. Mag. 4, 338, 1902.



which was stretched by a weight dipping in a vessel of water.

Heating was effected by means of an electric current. The heating coil was wound on a copper tube 40 cm long and 2.5 cm in



diameter well insulated with asbestos paper. The coil was wound anti-inductively two turns per centimeter by a wire about 1 mm thick. Two heating coils of the same dimensions were prepared, the one wound with a German silver wire and the other with a nickel wire. The former coil was used in the experiments below  $700^{\circ}\text{C}$  and the latter for higher temperatures. The melting point of nickel is about  $1500^{\circ}\text{C}$ , while its magnetic property is lost at a temperature below  $400^{\circ}\text{C}$ ; hence above this temperature, the presence of the metal does not at all disturb the magnetic field. By using a nickel wire for experiments at high temperature, we may dispense with a costly platinum wire or foil.

The heating coil was fixed by screws to the upper copper rod; while in its lower end was a hole, through which the lower copper rod passed without being in contact. The air current which might enter or escape through this narrow opening was

diminished on one side by another partition placed 5 cm above the lower end of the coil, and on the other side, by a bundle of fibrous asbestos attached to the copper rod just below the same end.

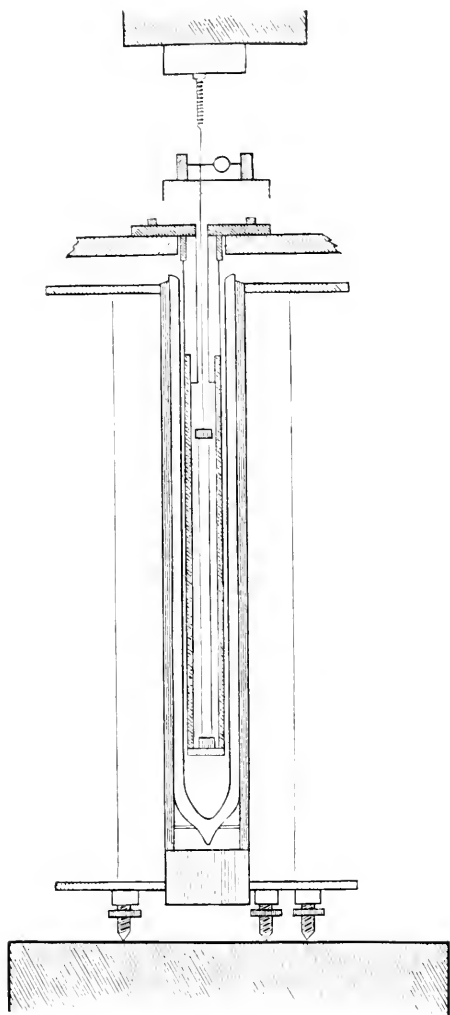
The exposed parts of the copper rods and wire were well covered with asbestos paper, except the part where the wire came in contact with the rotating cylinder. This precaution was necessary to diminish the loss of heat, and also to avoid the oscillating displacement of the image in the field of the telescope due to thermal expansion and contraction caused by the air current.

The temperature of the samples to be tested was measured by means of a platinum rhodium-platinum junction which was loosely placed in contact with the sample at its middle part, while the rest was insulated with asbestos paper. The other junction, also well insulated, was inserted into a copper tube dipped in a water bath of the temperature of the room. The thermoelectric current in the circuit was measured by a d'Arsonval galvanometer, and the constant of the pyrometer was determined by means of a mercury thermometer below 300°C, and by the melting points of zinc and sodium chloride above that temperature.

A magnetizing coil with a water-jacketed arrangement was placed co-axially with the suspended rod; it was 40 cm long and gave a field of 39.44 C.G.S. units at the center due to a current of one ampere.

When the adjustment was finished, the exposed parts were well covered with fibrous asbestos and cotton in order to diminish the loss of heat, care being taken to produce no sensible resistance to the elongation or contraction of our specimens.

For the measurement of the magnetic change of length in liquid air, the above arrangement was modified in the following way. The specimen was stretched upwards by means of a spiral spring,



instead of stretching it by a suspended weight. The shaded portions of the protruding holder were made of brass, while the unshaded part was made of wood to lessen the conduction of heat. Care was specially taken to stretch the copper wire in the direction of the axis of the rod.

The magnetizing coil with a Dewar's tube inside it, was placed co-axially with our rod. The contraction or elongation of the specimen was measured by the rotating cylinder in contact with a vertical copper wire. The temperature of liquid air was assumed to be  $-186^{\circ}\text{C}$ .

## § 2. METHOD OF OBSERVATION.

The experiments at low temperature were conducted in the following manner. The change of length at the temperature of the room was first determined and compared with the corresponding result obtained by the heating arrangement. The comparison showed

that these two results nearly coincided with each other. The liquid air was then gently poured into the Dewar's tube, until this tube was filled with the liquid, and the exposed parts above the magnetizing coil were carefully protected with cotton.

Owing to the boiling of the liquid, a small oscillation of the image in the field of the telescope was first observed ; but after about 10 minutes, the image became somewhat steady. The magnetic change of length was then measured in the usual way.

The experiment at high temperatures were undertaken in the following order. The magnetic change of length at the temperature of the room was first determined. Then an electric current from a dynamo was passed through the heating coil for one or two hours, till the temperature of the core became nearly constant ; then the current from the dynamo was replaced by one from an accumulator in order to get rid of the fluctuation of temperature due to that of the dynamo-current. Twenty or thirty minutes passed before the observations were taken, when the temperature had become very steady. The change of temperature caused a deflection of more than 6 cm per degree in the field of the observing telescope, whereas the deflection due to magnetization was utmost 5 cm in nickel and 1.5 cm in soft iron ; hence it can be easily conjectured how great difficulty is experienced in obtaining a constant temperature. Since the demagnetization was carefully effected before each observation and then an instantaneous deflection was noted, a slow displacement of the image, such as 1 mm in several minutes, could not cause any sensible error in the results. In our experiments, during the whole set of observations which usually required 10 or 15 minutes, the displacement of the zero point was only 2 or 3 mm except in a few cases.

If one set of observations was taken, a current of increased strength was again supplied by the dynamo for about an hour or

more, till, the temperature became nearly constant. The current-supply from the dynamo was then changed for that from the accumulator to repeat the same subsequent processes. In this way, experiments at successively increasing temperatures from the ordinary to the highest were carried out. Our heating coil gave a rise of temperature of about  $1000^{\circ}\text{C}$  in the core by passing a current of 11 amperes.

When the specimen was once heated to a high temperature, it underwent a permanent change with regard to the magnetic change of length ; thus it was necessary to try the experiment at low temperatures before our specimens had been heated to high temperatures.

The sensibility of our apparatus was such that an elongation or contraction of  $5 \times 10^{-8}$  of our specimens could easily be observed.

We tested 6 different samples shown in the following table :—

Metals	Length	Diameter	Demagnetizing factor
Soft iron	22.05 cm	1.025 cm	0.0683
Tungsten steel (rod)	22.93	0.940	0.0562
„ „ (prism)	22.00	$0.948 \times 0.953$	0.0751
Cast cobalt	22.10	1.044	0.0722
Ann. cobalt	22.03	1.083	0.0758
Nickel	22.03	1.121	0.0801

### § 3. RESULTS OF EXPERIMENTS.

The change of length of our specimen at the temperature of the room ( $8^{\circ}\text{C}$ – $17^{\circ}\text{C}$ ) is shown in Fig. 1.

The full lines represent the curves of the change of length plotted against the internal field ( $H' = H - IN$ ) ; the dotted lines refer to the external field. The comparison of the corresponding curves shows us the influence of the demagnetizing force.

In experiments at high temperatures, the internal field for a given magnetizing current varies with the temperature, as the intensity of magnetization changes with it. A full knowledge of the field in which experiments were carried on requires the determination of the intensity of magnetization at each temperature and field. Since our experiments did not extend so far, the curves of the length change at different temperatures were drawn for the external field. But if we refer to Fig. 1, it is easy to see how the forms of these curves are to be changed, if the effective field be used instead of the external one.

**Nickel.** The change of length in nickel under high and low temperatures is graphically shown in Fig. 2. The rise of temperature markedly reduces the magnetic contraction of the metal. At a temperature of  $240^{\circ}\text{C}$ , the contraction in  $H=800$  is already reduced to half its ordinary value, and at  $400^{\circ}\text{C}$ , it almost vanishes. With the ovoid of the same specimen, Professor H. Nagaoka and Mr. S. Kusakabe found the critical temperature to be  $400^{\circ}\text{C}$ . In liquid air, the contraction is reduced in weak fields, but is increased in strong fields. The relation between the change of length and the temperature for given external fields is given in Fig. 3. Each curve has a minimum point, the temperature of which decreases as the field is increased.

We also notice that the contraction vanishes asymptotically, as the temperature approaches to  $400^{\circ}\text{C}$ . It is to be remembered that on account of the demagnetizing force, each curve does not represent the contraction in a constant effective field, but shows the general feature of contraction with regard to temperature. The former results are consistent with the corresponding results in the present experiment.

**Soft iron.** The change of length in soft iron is given in Fig. 4. As the temperature is raised, the contraction in high fields

gradually disappears and at  $312^{\circ}\text{C}$ , the change of length is similar to that of tungsten steel at ordinary temperatures. With further increase of temperature, the elongation, after passing a maximum, gradually decreases. We could trace the elongation up to  $970^{\circ}\text{C}$ , which is far higher than its critical temperature. The effect of cooling by liquid air is considerably large in strong fields, producing an increase of contraction.

The relation between the change of length and the temperature is given in Fig. 5. It is remarkable to observe that the maximum elongation in weak fields which is characteristic for iron, remains almost constant for the temperatures ranging from  $-186^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ . Above this temperature, the elongation increases, till it reaches a maximum, and then rapidly decreases.

**Tungsten steel.** The results of experiments in tungsten steel are given in Figs. 6 and 7. The course of the curves and its change with temperature are similar to those of soft iron at temperatures higher than  $500^{\circ}\text{C}$ . The change of length seems to disappear nearly at the critical temperature, namely  $900^{\circ}\text{C}$ , a value obtained by Professor H. Nagaoka and Mr. S. Kusakabe. The former result obtained by one of us approximately agrees with the corresponding result in the present experiment.

With tungsten steel, we first studied the effect of temperature; when the specimen was cooled down to its initial temperature, it underwent a considerable permanent change with regard to the change of length. So the experiment in liquid air was performed with another rod of square section cut from the same specimen as the cylinder. The curves for  $10^{\circ}\text{C}$  and  $-186^{\circ}\text{C}$  are given in Fig. 8 which shows a slight effect of cooling on the change of length. Cooling decreases the elongation of the alloy in weak fields, but increases it in strong fields.

**Cast cobalt.** The results of observation in cast cobalt are drawn in Fig. 9. As the temperature is raised, the magnetic contraction in weak fields gradually lessens, and the elongation in strong fields increases, till it reaches a maximum. At temperatures higher than  $800^{\circ}\text{C}$ , the initial contraction altogether disappears and the course of the curves resembles that of iron and steel at high temperatures. If the temperatures be further increased, the elongation diminishes steadily, but at a diminishing rate, and even at such a high temperature as  $1020^{\circ}\text{C}$ , we still observe a considerable elongation of the metal. From the course of the curves in Fig. 10, it is easy to see that in  $H=800$ , the elongation does not vanish up to a temperature of  $1200^{\circ}\text{C}$ , which is higher than its critical temperature by  $100^{\circ}\text{C}$ . With our arrangement, it was not possible to push the experiments still further, as the melting point of copper was not far from that temperature. It is also to be observed that the field of maximum contraction gradually decreases as the temperature is raised, and that the temperature of maximum elongation in a given field diminishes as the field is increased.

With the same specimen, the effect of high temperature was first studied, and when the specimen was cooled down to its initial temperature, it totally changed its character with regard to the magnetic change of length. It was therefore not possible to examine the effect of cooling of the metal in the cast state.

**Annealed cobalt.** The specimen was annealed in a charcoal fire for about 4 hours, being carefully wrapped in asbestos papers. The effect of high temperatures on the magnetic change of length in annealed cobalt presents an extraordinary feature, as may be seen from Fig. 11. As the temperature is raised, beginning with that of liquid air, the contraction increases at first slowly and then rapidly, till it reaches a maximum. It then decreases and



after passing the state of no contraction, it is changed to an elongation, which again increases with the temperature up to a maximum, and then gradually diminishes. At such a high temperature as  $1034^{\circ}\text{C}$ , we could still observe a considerable elongation of the metal. To judge from the course of the curves, the temperature at which the elongation at last vanishes is nearly the same as in the cast cobalt. It is interesting to observe that the curve of the length change at a temperature near  $450^{\circ}\text{C}$  is similar to that of iron at ordinary temperature. The cobalt slightly elongates in weak fields ; but it contracts in strong fields. At a temperature higher than  $500^{\circ}\text{C}$ , the cast and annealed cobalts resemble each other in their behaviour in respect of the change of length.

The curves (Fig. 12) showing the relation between the change of length and the temperature, present a peculiar feature. They have generally a maximum point and a minimum ; in low fields, however, two small maxima and minima are observed. They also pass through a point ( $464^{\circ}\text{C}$ ) in the axis of the temperature. It follows then that there is a certain temperature, at which the change of length in the annealed cobalt nearly disappears for all magnetizing fields, and that the change occurs in an opposite sense in every field, according as the specimen is heated above or below that temperature. It appears then that annealed cobalt undergoes some molecular change at that temperature.

**General remarks.** On comparing the above results in soft iron, tungsten steel, cast and annealed cobalts, we notice the remarkable fact that the changes of length of these metals, at ordinary temperature so very different from each other, assume, at sufficiently high temperatures, an extraordinarily simple character ; they tend to become proportional to the magnetic force, a fact which has no doubt an important bearing in the theory of molecular magnetism. In Fig.

13, curves are drawn, one for each specimen, for the elongations at such temperatures that each specimen produces the same elongation in  $H=500$ . They all run very close to each other. It is also to be observed that the change of length at the critical temperature nearly disappears, and even in cases, in which we actually observe it, the amount of the change is a small fraction of that observed at ordinary temperatures.

In conclusion, let us give a short account of the permanent change with regard to the magnetic change of length. Cooling the specimens by liquid air generally produces no permanent effect on the length change at ordinary temperature; but heating it to a very high temperature produces a considerable permanent change. As seen from Fig. 14, the heating of annealed soft iron up to  $746^{\circ}\text{C}$  does not sensibly affect the change of length at ordinary temperature. Here the cross ( $\times$ ) denotes the points obtained after heating to  $746^{\circ}\text{C}$ . In tungsten steel, the effect is very large, tending to reduce the elongation in high fields (Fig. 15). In cast cobalt, the effect is still greater, changing totally the course of the curve, as seen from Fig. 16. If the specimen is once annealed at a high temperature, the subsequent heating and cooling between the same range of temperatures almost produce no effect on the change of length at ordinary temperature. But if the upper range of temperature be further increased, the change of length is slightly affected. This will be seen from the example of annealed cobalt (Fig. 17).

In the experiments at temperatures higher than  $700^{\circ}\text{C}$ , the suspended weight was reduced to 1 or 0.4 kilogram, according to circumstances. This was found necessary to avoid the gradual elongation of our specimens caused by the yielding at high temperatures.

It is hoped that the present investigation may be completed by studying the change of length in every stage of rising and falling

temperatures, and also by measuring the magnetization at the corresponding temperatures. The further extension to other ferromagnetics, such as nickel steels of different percentages, will also be undertaken in the near future.

## APPENDIX.

In the following tables,  $H$  denotes the external field,  $\frac{\partial l}{l}$  the change of length per unit of length by magnetization,  $l$  being the distance between two copper rods screwed to our ferromagnetics,  $t$  the temperature, and  $T$  the suspended weight.

## NICKEL.

$t = -186^\circ$		$t = 17.2^\circ, T = 2kg.$		$t = 69^\circ, T = 2kg.$		$t = 143^\circ, T = 2kg.$	
$H$	$\frac{\partial l}{l} \times 10^6$	$H$	$\frac{\partial l}{l} \times 10^6$	$H$	$\frac{\partial l}{l} \times 10^6$	$H$	$\frac{\partial l}{l} \times 10^6$
18	- 0.61	12	- 0.93	13	- 0.93	12	- 1.00
37	- 3.90	35	- 5.64	35	- 5.26	35	- 4.79
62	- 9.33	59	- 11.90	59	- 10.36	60	- 9.42
89	- 14.00	87	- 17.78	86	- 15.85	88	- 13.75
123	- 18.20	154	- 26.38	151	- 23.58	152	- 19.55
212	- 24.32	207	- 30.08	205	- 26.65	204	- 21.58
290	- 26.76	282	- 32.60	279	- 29.20	279	- 23.02
395	- 29.68	384	- 34.62	378	- 31.00	382	- 24.04
557	- 32.88	535	- 35.61	541	- 31.30	542	- 25.50
733	- 35.77	706	- 36.42	712	- 32.08	715	- 26.03
910	- 37.38	868	- 37.00	878	- 32.20	870	- 26.52

$t = 197^\circ, T = 2kg.$		$t = 261^\circ, T = 2kg.$		$t = 346^\circ, T = 2kg.$		$t = 376^\circ, T = 2kg.$	
$H$	$\frac{\partial l}{l} \times 10^6$	$H$	$\frac{\partial l}{l} \times 10^6$	$H$	$\frac{\partial l}{l} \times 10^6$	$H$	$\frac{\partial l}{l} \times 10^6$
16	- 1.39	15	- 1.39	12	- 0.62	12	- 0.08
36	- 4.79	35	- 4.72	23	- 1.31	—	—
59	- 8.81	59	- 7.58	35	- 2.01	35	- 0.15
85	- 12.45	87	- 9.89	59	- 2.55	59	- 0.23
120	- 15.38	153	- 11.82	85	- 2.76	87	- 0.46
204	- 18.40	200	- 12.60	152	- 3.17	152	- 0.54
278	- 19.40	277	- 13.21	282	- 3.63	282	- 0.58
382	- 20.02	381	- 13.21	382	- 3.63	382	- 0.54
534	- 20.40	531	- 13.29	538	- 3.63	542	- 0.54
706	- 20.93	702	- 13.52	706	- 3.71	715	- 0.54
870	- 21.02	868	- 13.60	868	- 3.71	875	- 0.54

## SOFT IRON.

$t = -186^\circ$		$t = 8.4^\circ, T = 1kg.$		$t = 168^\circ, T = 1kg.$		$t = 319^\circ, T = 1kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
37	1.36	24	0.39	24	0.16	23	0.39
60	2.27	60	2.09	63	1.55	62	2.79
89	3.25	90	3.10	94	3.10	92	4.34
124	3.18	110	3.18	115	3.33	112	4.65
—	—	139	3.10	146	3.33	143	4.73
210	1.89	215	2.17	224	2.87	218	4.65
286	0.00	292	0.69	300	1.71	294	4.03
393	— 2.34	387	— 0.93	404	0.39	406	3.64
559	— 5.45	570	— 3.53	584	— 1.55	569	2.87
738	— 7.63	757	— 5.42	769	— 2.25	757	2.33
894	— 9.08	932	— 6.28	947	— 3.10	925	2.17

$t = 559^\circ, T = 1kg.$		$t = 746^\circ, T = 0.4kg.$		$t = 818^\circ, T = 0.4kg.$		$t = 882^\circ, T = 0.4kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
24	0.46	23	0.47	36	0.00	—	—
62	3.26	61	1.86	—	—	—	—
113	5.43	111	2.32	99	0.08	—	—
184	5.81	182	3.10	—	—	—	—
292	6.20	289	3.88	253	0.70	268	0.12
389	6.20	392	4.18	365	1.01	—	—
564	6.20	558	4.26	561	1.55	493	0.23
743	5.81	732	4.65	737	1.78	725	0.70
913	5.66	896	4.65	898	2.17	881	0.97

## TUNGSTEN STEEL.

Square prism.

Circular cylinder.

$t = -186^\circ$		$t = 10.0^\circ$		$t = 11.5^\circ, T = 2kg.$		$t = 225^\circ, T = 2kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
—	—	36	0.23	36	0.23	36	0.46
60	0.76	61	0.92	60	1.52	60	1.90
108	2.59	109	3.20	108	3.61	108	3.66
176	3.89	168	4.58	179	4.41	179	4.11
277	4.65	276	4.73	277	4.72	277	4.57
370	4.42	371	4.58	369	4.72	366	4.57
562	3.89	571	3.97	571	4.34	562	4.34
748	3.66	753	3.28	747	4.03	744	4.00
921	3.20	923	2.98	925	3.73	911	3.88

$t = 410^\circ, T = 2kg.$		$t = 592^\circ, T = 1kg.$		$t = 722^\circ, T = 1kg.$		$t = 828^\circ, T = 1kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
36	0.53	36	1.22	37	0.30	—	—
60	2.13	61	2.13	60	0.76	—	—
108	2.89	108	2.97	107	1.22	—	—
177	3.80	174	3.58	171	1.45	—	—
276	4.03	273	4.34	277	2.06	271	0.08
363	4.34	362	4.50	360	2.44	—	—
558	4.46	554	4.95	549	2.59	552	0.23
732	5.10	720	5.18	708	3.04	723	0.46
888	5.40	891	5.33	867	3.20	881	0.76

## CAST COBALT.

$t=17.3^\circ, T=2kg.$		$t=80^\circ, T=2kg.$		$t=155^\circ, T=2kg.$		$t=281^\circ, T=2kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10$
23	- 0.55	22	- 0.47	22	- 0.47	23	- 0.55
35	- 1.49	36	- 1.45	36	- 1.37	35	- 1.38
60	- 3.92	60	- 3.76	60	- 3.33	60	- 2.98
88	- 6.35	88	- 5.72	88	- 5.25	89	- 3.92
122	- 7.68	122	- 6.58	123	- 5.40	123	- 3.14
154	- 7.76	153	- 6.40	154	- 4.86	155	- 1.80
210	- 6.47	206	- 5.53	208	- 2.94	208	+ 0.62
284	- 4.31	282	- 2.43	283	+ 0.16	282	+ 4.62
388	- 1.02	388	+ 1.25	388	+ 4.55	385	+ 8.62
542	+ 3.68	542	+ 6.35	539	+ 9.16	545	+ 13.87
708	+ 7.76	720	+ 10.50	710	+ 13.20	715	+ 17.40
866	+ 10.80	874	+ 13.32	883	+ 15.82	882	+ 19.73

$t=515^\circ, T=2kg.$		$t=746^\circ, T=0.4kg.$		$t=911^\circ, T=0.4kg.$		$t=1020^\circ, T=0.4kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
24	- 0.27	24	+ 0.19	—	—	—	—
35	- 0.55	48	+ 0.78	48	+ 2.28	—	—
59	- 0.94	—	—	—	—	—	—
87	- 0.08	—	—	—	—	—	—
121	+ 2.35	110	+ 4.12	108	+ 4.73	—	—
206	+ 7.44	182	+ 8.54	247	+ 7.10	—	—
280	+ 10.97	289	+ 12.03	—	—	—	—
376	+ 12.46	395	+ 14.38	448	+ 9.07	370	+ 2.76
534	+ 18.02	559	+ 16.30	663	+ 10.10	677	+ 3.71
689	+ 20.61	732	+ 17.86	—	—	—	—
845	+ 22.36	903	+ 18.63	879	+ 10.64	903	+ 3.94

## ANNEALED COBALT.

$t = -186^\circ$		$t = 9.0^\circ, T = 2kg.$		$t = 166^\circ, T = 2kg.$		$t = 234^\circ, T = 1kg,$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
—	—	—	—	—	—	36	— 0.54
60	— 0.08	65	— 0.19	60	— 0.31	62	— 1.02
108	— 0.16	110	— 0.78	115	— 1.41	112	— 2.97
174	— 0.71	161	— 1.56	161	— 2.54	183	— 6.10
275	— 1.57	298	— 2.97	295	— 4.69	292	— 9.61
370	— 2.52	398	— 4.06	399	— 6.88	398	— 12.98
562	— 4.09	586	— 5.86	581	— 9.30	561	— 16.80
739	— 6.29	757	— 7.81	762	— 11.95	749	— 19.52
906	— 7.86	937	— 9.45	932	— 14.14	911	— 21.64

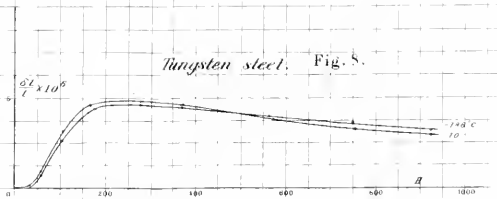
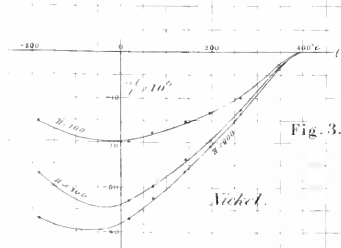
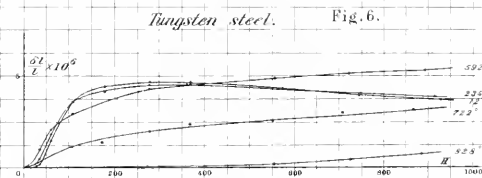
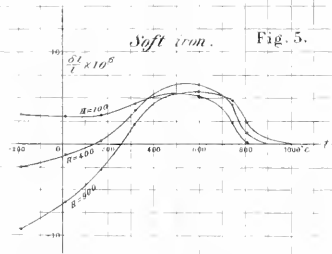
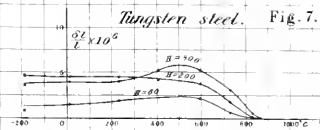
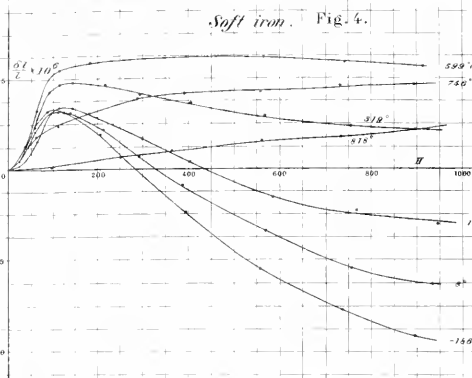
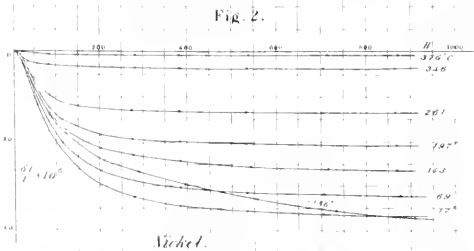
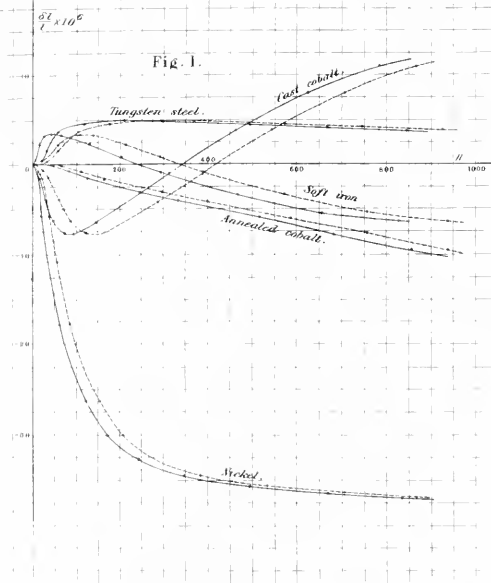
$t = 291^\circ, T = 2kg.$		$t = 413^\circ, T = 2kg.$		$t = 451^\circ, T = 2kg.$		$t = 505^\circ, T = 2kg.$	
$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
34	— 0.98	39	+ 0.15	37	+ 0.19	37	— 0.23
62	— 3.28	62	+ 0.08	62	+ 0.31	62	— 0.70
115	— 6.25	110	0.00	112	+ 0.63	112	— 0.62
181	— 10.16	181	— 1.49	181	+ 0.63	182	+ 0.55
295	— 13.75	289	— 3.52	291	— 0.08	290	+ 2.97
398	— 15.62	395	— 5.47	397	— 1.02	395	+ 4.69
575	— 17.23	562	— 8.52	566	— 2.35	564	+ 6.18
749	— 17.90	737	— 10.00	740	— 3.83	732	+ 7.19
920	— 18.60	911	— 11.56	911	— 4.69	910	+ 7.97



$t=592^{\circ}, T=1kg.$		$t=767^{\circ}, T=1kg.$		$t=943^{\circ}, T=1kg.$		$t=1034^{\circ}, T=0.4kg$	
$H$	$\frac{\delta l}{l} \times 10$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$	$H$	$\frac{\delta l}{l} \times 10^6$
36	- 0.19	36	0.00	36	+ 0.23	—	—
60	- 0.47	60	+ 0.19	89	+ 1.95	—	—
111	- 0.16	110	+ 1.95	—	—	124	+ 0.54
181	+ 2.11	179	+ 4.07	175	+ 3.90	—	—
290	+ 5.63	287	+ 7.20	333	+ 5.47	271	+ 1.72
392	+ 7.81	389	+ 9.00	—	—	—	—
560	+10.39	562	+11.10	610	+ 7.27	493	+ 2.34
738	+12.42	732	+12.50	+	—	717	+ 2.74
903	+13.13	898	+13.20	906	+ 7.97	878	+ 3.36









*Cast cobalt.* Fig. 9.

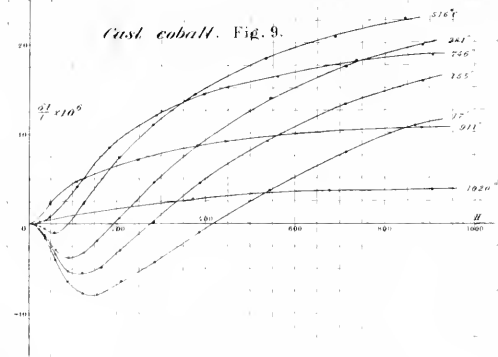


Fig. 10.

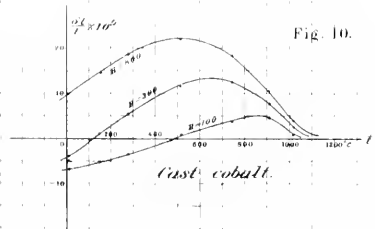
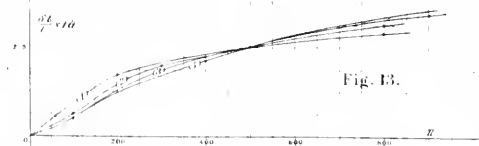
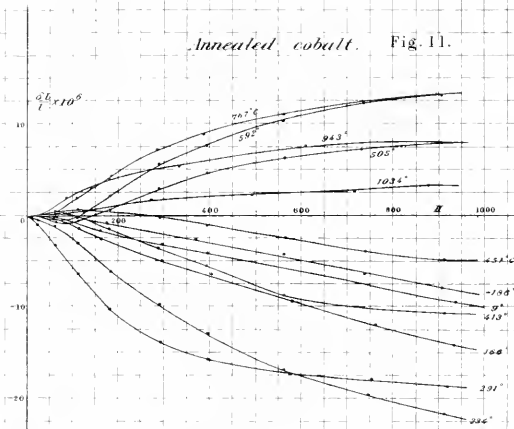


Fig. 13.



- (1) Tungsten steel, 725°C; (2) Soft iron, 788°C.  
(3) Cast cobalt, 1034°C; (4) Ann. cobalt, 1032°C.

*Annealed cobalt.* Fig. 11.



*Annealed cobalt.*

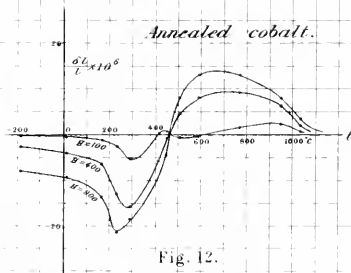
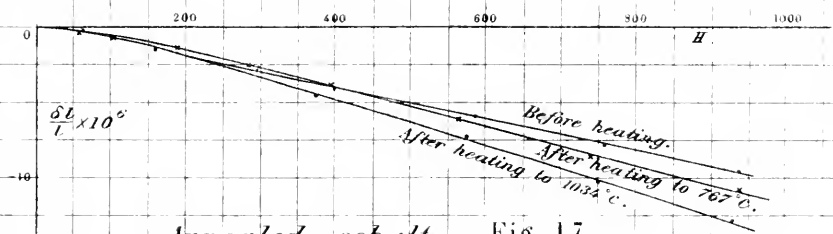
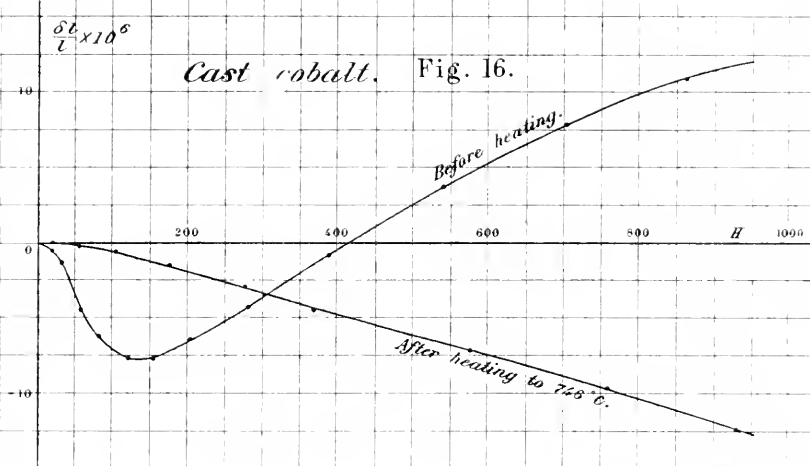
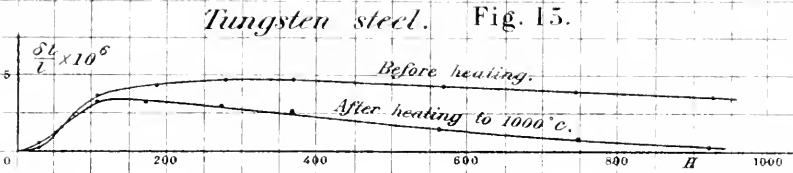
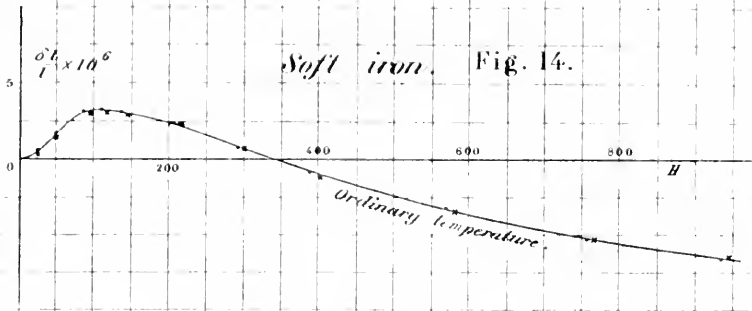


Fig. 12.









## Magnetization and Magnetostriction of Nickel Steels, containing different Percentages of Nickel.

By

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*With Plates I—III.*

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The results of our experiments<sup>1)</sup> on the magnetostriction of nickel steels have been discussed by Guillaume<sup>2)</sup> and Osmond.<sup>3)</sup> The samples, which we had then tested, were only four in number, so that no definite conclusion as regards the effect on magnetostriction by varying the percentage content of nickel could be drawn. Having now examined eight new specimens,<sup>4)</sup> we are able to infer how the magnetization and the magnetostriction go on varying as the proportion of nickel to iron is increased. The importance of investigat-

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1) Nagaoka and Honda, *Comptes Rendus*, 3 Mars, 1902; *Journal de physique*, Octobre 1902.

2) Guillaume, *Comptes Rendus*, 3 Mars, 1902.

3) Osmond, *Comptes Rendus*, 17 Mars, 1902.

4) Our thanks are due to Mr. Ch. Ed. Guillaume, at whose kind request, the Company of Commentry-Fourchambault and Decazeville has liberally supplied us with specimens.

ing the magnetostriction of these valuable alloys appears from the following words of Mons. L. Dumas in his report on researches concerning nickel steels.

“M. Guillaume, d'autre part, a fait remarquer que notre hypothèse ne fournit aucune base pour l'interprétation des phénomènes de magnetostriction, signalés par Mess. Nagaoka et Honda comme constatés sur des aciers au nickel qui ont été mis à leur disposition par Imphy. Tel est l'état actuel de cette intéressante question.” We hope that the present experiment will give some clue to a theory, which will explain not only the thermal, electrical, and magnetic behaviour of the metal, but also various metallurgical and mechanical properties.

*Method of experiment.*—The nickel steel rods were all turned into ovoids ( $2a=20$  cm.,  $2b=1$  cm.), and placed axially in a coil (30 cm. long, 0.6 Ohm resistance,  $4\pi n=379.7$ ). The magnetization was determined by means of a magnetometer, the effect of the coil being compensated by means of another coil of the same strength placed symmetrically on the other side of the magnetometer. The change of length was measured by means of an apparatus described in the Philosophical Magazine, February, 1894, and in this journal Vol. 16, Art. 8. The ovoids were sealed in dilatometer, and the change of volume measured by the displacement of the capillary meniscus. In all these experiments, the utmost care was taken to eliminate the effect of heating by waterjacketing the coil, and by observing the displacement, a few seconds after making the magnetizing current. The ovoids were demagnetized by the method of reversals of gradually decreasing currents before each observation.

*Magnetization of nickel steels.*—From experiments made with eight different specimens of nickel steels, varying from 26.2 to 44 percent of nickel, Dumont<sup>1)</sup> found a gradual increase of susceptibility

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1) Dumont, Comptes Rendus, p. 741, tom. 76, 1898.

as the amount of nickel became greater. The range of percentage difference in nickel was greater in the present experiment, so that some singular features in the course of the magnetization curves were revealed.<sup>1)</sup>

The following table gives the observed magnetizations in different fields :—

70.32%		50.72%		46%	
$\mathfrak{H}$	$\mathfrak{J}$	$\mathfrak{H}$	$\mathfrak{J}$	$\mathfrak{H}$	$\mathfrak{J}$
0.24	9	0.42	9	0.29	7
1.52	120	1.86	58	2.30	79
3.90	500	2.92	207	3.02	175
5.60	576	4.13	489	4.08	279
11.30	720	8.81	726	4.92	362
32.6	902	12.78	868	5.88	473
63.5	967	24.50	1013	7.22	592
91.6	986	36.6	1074	8.22	684
168.4	1000	51.6	1135	11.10	793
232.4	1000	73.3	1178	17.15	909
299.4	1002	146.7	1222	33.8	1054
381	1003	252.4	1240	91.1	1171
451	1004	329	1241	266.7	1214
576	1006	520	1246	372	1219
672	1008	606	1249	533	1222

1) The percentages of nickel were given by Imphy.

36%		29.42%		29%	
₤	₯	₤	₯	₤	₯
1.27	32	0.68	12	1.00	11
2.45	73	1.58	41	2.95	131
3.07	123	2.46	66	7.60	207
4.00	176	4.41	92	19.60	272
5.86	345	9.90	118	—	—
9.50	524	22.40	138	—	—
11.55	624	35.3	147	—	—
16.05	714	43.7	150	67.1	307
30.4	853	83.6	160	—	—
65.1	953	135.7	164	143.7	315
110.5	989	210.5	174	244	321
203.5	1007	324	181	399	328
350	1012	440	189	515	333
473	1013	504	193	532	333
662	1014	657	201	738	341

28.72%		28.32%		26.64%	
$\delta$	$\mathfrak{J}$	$\delta$	$\mathfrak{J}$	$\delta$	$\mathfrak{J}$
0.29	6	0.52	6	—	—
1.61	70	2.42	23	—	—
4.20	156	6.40	37	23.5	2.0
13.70	242	14.58	48	—	—
29.2	278	24.24	53	—	—
46.2	292	43.1	58	70.5	5.2
87.0	305	97.2	69	119.3	8.0
159.4	313	206.0	84	219.1	11.8
233.4	318	327	98	356	15.2
407	325	596	119	493	17.5
474	326	672	126	626	19.5
675	331	752	128	750	21.2

24.40%		24.04%	
$\delta$	$\mathfrak{J}$	$\delta$	$\mathfrak{J}$
—	—	7.56	3
29.5	1.9	14.20	7
—	—	33.8	14
71.0	3.4	52.8	22
126.2	5.4	141.3	42
230.4	7.8	226.6	53
412	9.3	407	68
541	10.6	536	76
653	10.8	626	80
769	11.5	763	85

The greatest field (external field — demagnetizing factor  $\times$  intensity of magnetization)<sup>1)</sup> is about 700 Gauss. For this strength, nearly all the alloys here studied become saturated, so that further increase of the field would have been superfluous. As found by Hopkinson, the magnetization of 25 per cent Ni. is almost nil, while it increases as the content of nickel is increased or decreased. For want of material, the magnetization for percentages of nickel lower than 24.04 was not studied. For 29 per cent Ni., the magnetization attains a maximum value, thence to decrease with the increase of nickel. This decrease is, however, of very small amount, so that after reaching a minimum, the magnetization shows rapid increase and tends towards a maximum as the percentage of nickel becomes nearly equal to that of iron. Thus the magnetization curve for 46 per cent Ni. lies a little below that for 50.72 per cent Ni. The percentage content of nickel, which shows maximum susceptibility, becomes smaller as the field is increased, ultimately tending towards 50 per cent as will be seen in Fig. 2. From this maximum, the susceptibility gradually diminishes, so that the magnetization curves for 36 per cent and 70.32 per cent are nearly coincident, as shown in Fig. 1. In the descending branches of the curves of susceptibility, there is apparently no such singularity as in the ascending portion. An inspection of Fig. 2. will show how the magnetization varies as the percentage of nickel is gradually increased. It is evident that the intensity of magnetization does not follow the law of simple proportion to the specific magnetizations of the respective metals.

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1) It is to be noticed that in all of our former experiments, we had taken the demagnetizing factor ( $=0.836$ ) into account.

*Change of length by magnetization.*—The following table gives the observed changes of length :

70.32%		50.72%		46%	
$\mathfrak{H}$	$\frac{\delta l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\delta l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\delta l}{l} \times 10^6$
5.3	0.8	4.1	0.6	4.6	0.2
9.5	1.9	24.2	5.4	6.7	0.9
17.8	3.3	43.5	7.7	10.6	2.6
86.2	6.9	113.6	12.5	32.2	9.7
269.6	7.5	250.6	15.4	71.1	15.9
401	7.6	327	16.3	121.2	18.7
681	7.6	436	16.9	314	22.3
990	7.3	838	18.2	573	23.3
1155	7.2	1090	18.1	860	23.9
1537	7.1	1466	17.9	1508	24.8

36%		29.42%		29%	
$\mathfrak{H}$	$\frac{\delta l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\delta l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\delta l}{l} \times 10^6$
7.5	0.4	18.6	0.0	15.0	0.1
17.6	2.0	42.0	0.3	27.8	0.9
37.1	5.1	99.0	0.7	45.3	1.1
151.5	12.3	200.0	1.5	81.8	1.7
234.0	13.7	338	2.2	135.7	2.3
341	14.8	530	3.4	292.2	3.6
587	16.2	724	4.8	510	5.5
1050	18.3	1032	6.9	864	8.6
1342	19.8	1292	8.4	1238	12.2
1905	22.1	1556	10.2	1622	15.2

28.72%		28.32%		26.64%	
$\mathfrak{H}$	$\frac{\partial l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\partial l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\partial l}{l} \times 10^6$
28.9	0.3	36.0	0.0	—	—
85.3	0.9	39.0	0.0	—	—
144.6	1.5	179.0	0.1	—	—
264.7	2.1	403	0.4	—	—
461	3.5	513	0.7	236	0.0
710	5.2	710	1.2	671	0.1
896	6.7	1025	2.0	882	0.2
1155	9.3	1340	2.9	—	—
1532	12.6	1861	4.5	1850	0.4

24.40%		24.04%	
$\mathfrak{H}$	$\frac{\partial l}{l} \times 10^6$	$\mathfrak{H}$	$\frac{\partial l}{l} \times 10^6$
—	—	89	0.0
186	0.00	181	0.1
—	—	288	0.4
407	0.02	414	0.7
683	0.04	688	1.3
988	0.07	1045	1.8
1419	0.07	1508	2.4
1867	0.09	1877	2.8

All the nickel steels hitherto examined show increase of length. The behaviours of the alloys containing 24.04 to 46 per cent are similar as regards the change of length, and do not indicate the existence of maximum elongation up to 2000 Gauss. It is, however, to be remarked that the rate of increase diminishes as the percentage



increases. Ultimately, with further additions of nickel, the maximum elongation makes its appearance, and is already present for 50.72 per cent in field of 1000 Gauss; with 70.32 per cent Ni., this occurs in  $\mathfrak{H}=170$ . It thus appears that the increase of nickel beyond 50 per cent displaces the maximum point in the direction of the lower field. In fact, the character of the change resembles that in iron. With further additions of nickel, the metal will show contraction, which goes on increasing with the field. This remarkable change in the character of elongation will probably occur, when the metal approaches pure nickel. Further it is to be noticed that the elongation in all these specimens exceeds that of the constituent ferromagnetics.

An examination of Fig. 4 discloses how the transition between the elongation in iron and the contraction in nickel takes place. The curves of elongation plotted against the percentage content of nickel are similar to those of magnetization, showing two maxima and two minima between 24 per cent and 50 per cent of nickel. The alloy indicating the maximum elongation is little greater than 40 per cent, which nearly coincides with that showing greatest susceptibility.

*Change of volume by magnetization.*—The observed changes of volume are given in the following tables :—

70.32%		50.72%		46%	
$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$
2	−0.00	5	0.05	68.1	0.03
57	−0.06	47	0.09	284.5	0.42
86	−0.04	75	0.11	386	0.69
158	−0.01	272	0.34	592	1.13
339	+0.08	443	0.54	679	1.28
635	+0.23	688	0.90	893	1.59
808	+0.29	985	1.35	994	2.19
1212	+0.46	1197	1.79	1327	3.00
—	—	1322	1.84	1452	3.55
1614	+0.63	1607	2.46	1618	4.38

36%		29.42%		29%	
$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$
7.6	0.03	19	0.38	6.5	0.06
11.8	0.05	35	1.25	25.7	0.71
30.8	0.24	88	2.93	62.4	1.49
93.5	0.87	153	4.91	113.6	2.91
209.1	2.35	333	10.5	227.5	6.52
309	4.28	517	16.3	425	12.5
682	9.10	765	23.2	659	20.3
1042	14.3	979	29.3	989	29.7
1333	18.4	1370	39.9	1260	38.7
1669	23.0	1685	47.4	1687	51.1

28.72%		28.32%		26.64%	
$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$
25	0.55	24	0.27	—	—
76	2.20	38	0.34	—	—
142	4.25	89	0.90	—	—
257	7.73	176	1.67	179	0.07
449	14.2	384	3.95	392	0.27
666	20.3	530	5.86	—	—
857	25.6	632	7.20	635	0.69
1076	31.6	920	11.1	929	0.96
1355	39.8	1315	16.8	1318	1.76
1662	47.6	1636	21.4	1640	2.65

24.40%		24.04%	
$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$	$\mathfrak{H}$	$\frac{\delta v}{v} \times 10^6$
176	0.00	175	0.04
387	0.02	391	0.14
641	0.07	640	0.17
925	0.17	942	0.30
1325	0.23	1351	0.55
1651	0.27	1671	0.69

As has been already noticed in the previous contribution, the increase of volume in nickel steels by magnetization is nearly proportional to the strength of the field. The change is enormously large compared with that in the constituent metals iron and nickel. The maximum effect is observed in 29 per cent Ni., being about

$50 \times 10^{-6}$  in a field of 1600 Gauss. We noticed a slight decrease of volume for 70.32 per cent Ni. specimen in weak fields.

Plotting the volume change in constant fields (Fig. 6) against the percentage content of nickel, we notice a sudden ascent for 25 per cent to 29 per cent, and then a sudden descent to about 40 per cent. The decrease in the volume change becomes gradually less as the alloy approaches pure nickel.

On several occasions, we have remarked that the volume change by magnetization is of a differential nature, since

$$\text{Volume change in void} = \text{elongation parallel to magnetization} \\ + 2 \cdot \text{elongation perpendicular to magnetization.}$$

Generally, the elongation in the direction of magnetization is of opposite sign to that in the direction perpendicular to it. In iron and nickel, the sum of these elongations representing the volume change nearly vanishes, while in nickel steels, this is by no means the case. The sum of these respective elongations is maximum in 29 per cent Ni., in which the position of maximum effect is very prominent. The phenomenon is the more remarkable as this point nearly coincides with the corresponding points for magnetization and elongation by magnetization. The border line which marks the transition of nickel steel from *acier dur* to *acier doux* is also little short of the same percentage, which will probably explain the existence of the maximum change of volume, considered as a differential effect.

*Connexion with other physical properties of nickel steel.*—When we examine various other physical properties of this valuable alloy, we cannot but be struck with the singular coincidence of the changes attending the magnetization in the neighbourhood of 29 per cent Ni. with those attending the elastic and thermal behaviour as the metal is transformed from *acier dur* to *acier doux*. For the said percentage content of nickel, the resistance to rupture is least, but the elongation on

the application of breaking stress is maximum ; it is for about the same percentage that the irreversible metal can be made reversible, while the temperature of transformation by cooling becomes very low ; and for the same percentage, the rate of decrease of the thermal coefficient of expansion due to the addition of nickel is the greatest.

These coincidences do not appear to be merely accidental and further researches as to electric and thermal conductivities will probably reveal similar singularities in the same region. A really satisfactory theory of the constitution of the alloy must explain, not only the metallurgical aspect of the metal, but also its various physical characteristics, and unite them in a common bond. For this purpose, different investigations by changing the conditions under which the metal is tested, will give valuable clues to the exposition of a theory





Fig. 1.

*Magnetization of Nickel Steels.*

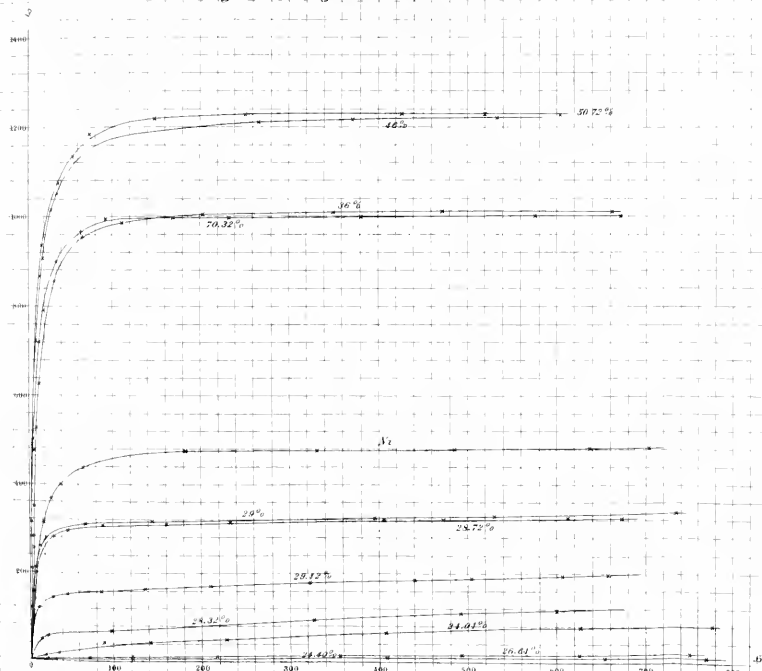


Fig. 2.

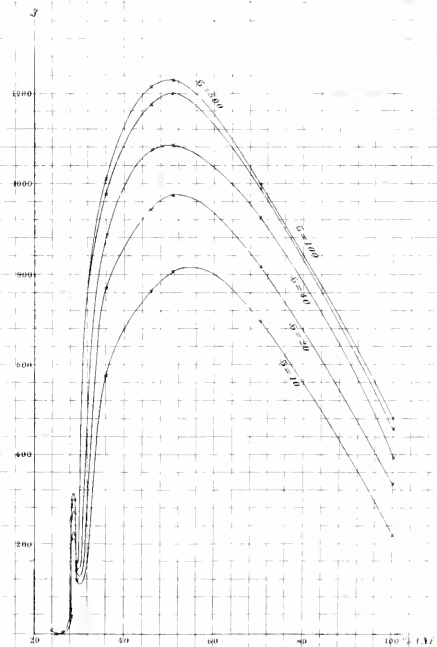






Fig. 3.

*Length Change of Nickel Steels.*

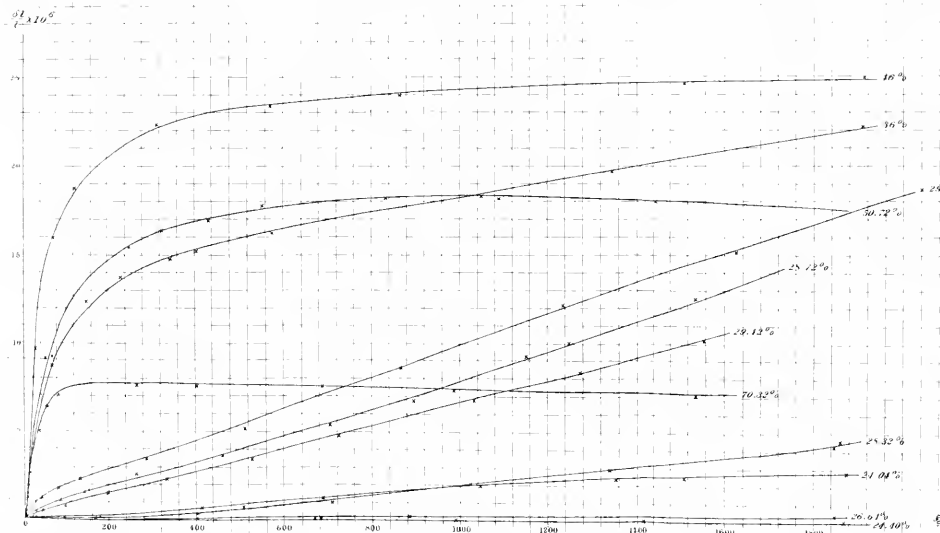
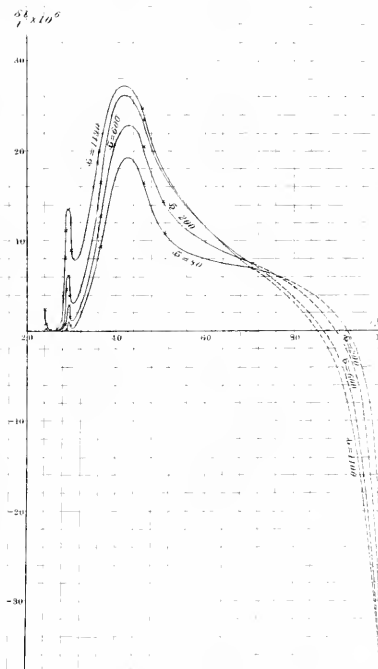


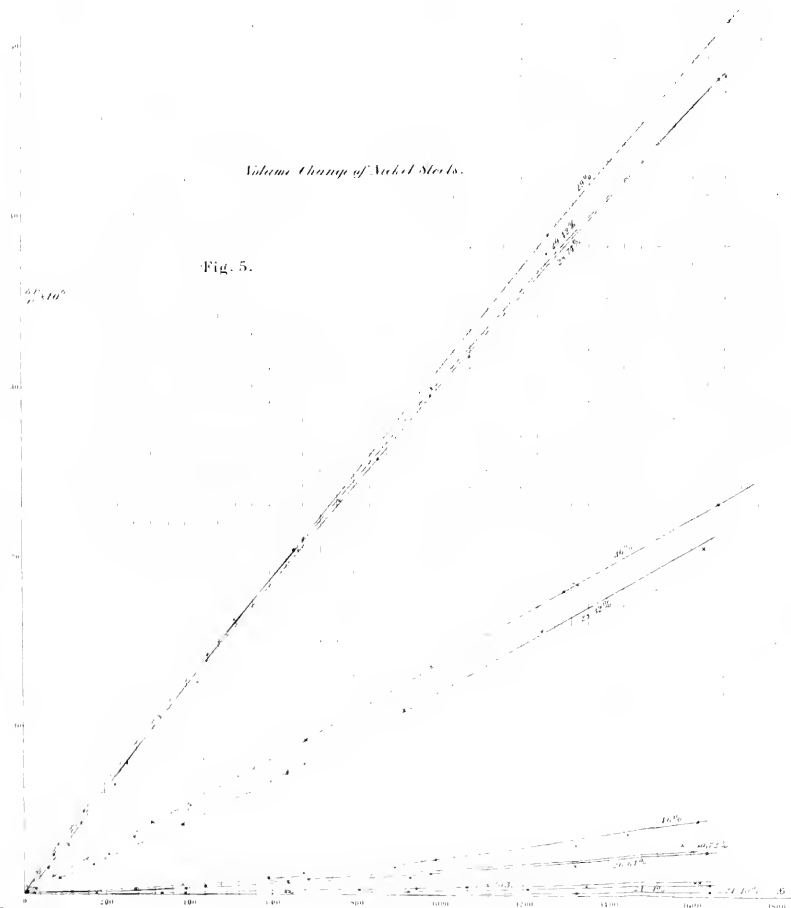
Fig. 4.





*Volume Change of Nickel Sulfide.*

Fig. 5.



$\Delta V \times 10^6$

500

400

300

200

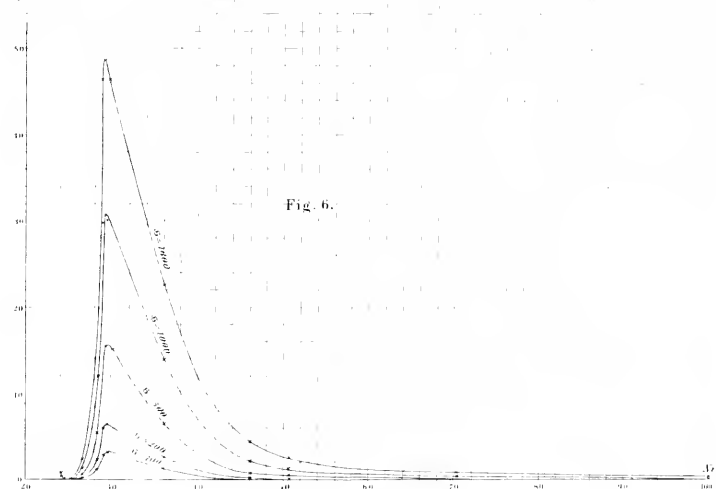
100

0

0

0

Fig. 6.





## The Composition of so-called Elæomargaric Acid.

By

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The oil of *Elæococca vernicia*, or Japanese wood oil, was first investigated by S. Cloëz (*Compt. rend.*, 1875, **81**, 469 : 1876, **82**, 501 ; 1876, **83**, 943), who, on saponifying the oil with alcoholic potash, obtained two acids, one of which was solid and the other liquid at the ordinary temperature. At first, he gave the formula  $C_{17}H_{30}O_2$  to the solid acid, which he named *margarolic acid*, but in his third paper he changed the formula to  $C_{17}H_{30}O_2$ , having found that the earlier formula was incorrect owing to some absorption of oxygen by the acid having been overlooked. He also changed the name of the acid to *elæomargaric acid*. The liquid acid, which he at first named *oleic acid*, was afterwards found to be ordinary oleic acid, the oil containing about 75 per cent. of the glyceride of elæo-margaric acid and 25 per cent. of olein.

From the analysis and the determination of the neutralisation number, K. Ishikawa (*Dissertation*, 1885, unpublished) gave the formula  $C_{17}H_{28}O_2$  to the solid acid, whilst De Negri and Sburlati (*L'Orosi*, 1896, **19** 291) adopted Cloëz's formula,  $C_{17}H_{30}O_2$ .

In 1899, K. Higuchi (*Journ. Chem. Ind., Tokyo*, **2**, 1), by

oxidising the solid acid with potassium permanganate in an alkaline solution, obtained, besides dihydrostearic acid, a product which resembled sativic acid in many respects, but which he did not further examine. Quite recently, L. Maquenne (*Compt. rend.*, 1902, **135**, 696) has published a paper "On the solid acid from the oil of *Elaeococca vernicia*," in which he endeavoured to show that the composition of the acid is  $C_{18}H_{30}O_2$  rather than  $C_{17}H_{30}O_2$  as given by Cloëz, and that the acid must therefore be stereoisomeric with linolenic acid. He arrived at this conclusion merely from the analysis of the acid, and stated that on account of the acid not forming any definite derivatives, its composition cannot be established by indirect means, his attempt to prepare the bromine additive product having failed.

The present communication is a preliminary report of an investigation, begun in 1901 and still in progress, which has for its object the determination of the composition of the acids of the oil by studying their oxidation and bromine additive products.

Although the work is still incomplete, it is desirable, in view of the appearance of Maquenne's paper, that the results should at once be published. A bromine additive product having the formula  $C_{18}H_{32}O_2Br_4$  was prepared without any difficulty from the mixture of acids produced by saponifying the oil, and from the recrystallised solid acid were isolated oxidation products having the formulae  $C_{18}H_{32}(OH)_4O_2$  and  $C_{18}H_{34}(OH)_2O_2$ , but no derivatives of either of the acids  $C_{17}H_{30}O_2$  or  $C_{18}H_{30}O_2$  could be obtained.\* If the acid  $C_{18}H_{30}O_2$  had been present in the mixture, as is asserted by Maquenne, the oxidation product,  $C_{18}H_{30}(OH)_6O_2$ , might have been expected, and should have been obtained in the course of a systematic separation of the products of oxidation (see experimental part). The principal acids of the oil

\* In confirmation of the statement that no hexabromide can be obtained, see Walker and Warburton in the *Analyst*, 1902, **27**, 238.

appear, therefore, to be oleic acid and a solid acid having the formula  $C_{18}H_{32}O_2$ , stereoisomeric with linolic acid, whilst the presence in any considerable quantity of the acid  $C_{18}H_{30}O_2$  is excluded. The determination of the neutralisation number of the solid acid by means of carefully standardised alkali shows, moreover, that this corresponds with the formula  $C_{18}H_{32}O_2$  rather than with  $C_{17}H_{32}O_2$ .

No attempt was made to repeat the analyses of the solid acid, since no definite information was to be expected from the result on account of the small difference in the percentage amounts of carbon and hydrogen required by the formulæ  $C_{18}H_{32}O_2$ ,  $C_{18}H_{30}O_2$ , and  $C_{17}H_{30}O_2$ . The silver and lead salts of the solid acid were prepared, but they are both amorphous and very readily oxidisable in the air, even more so than the acid itself, so that, although silver estimations were made, no concordant results could be obtained. The reduction of the solid unsaturated acid by heating in a sealed tube with fuming hydriodic acid and red phosphorus has been tried, but the experiments in this direction have not yet been brought to a successful issue.

### *Experimental.*

*Saponification of the Oil.*—To 30 grams of the cold-drawn oil contained in a flask were added 100 c.c. of alcohol and 15 grams of caustic potash, dissolved in 60 c.c. of water. The flask was connected with an inverted condenser and the contents gently boiled on the water-bath for about two hours. Hydrochloric acid was then added, in slight excess, to the clear alcoholic solution, when a brown oil separated, changing into a crystalline mass on cooling. By recrystallisation from alcohol, the solid acid was obtained in the form of white, lustrous laminae melting at  $43\text{--}44^\circ$  (Cloëz gives the melting point of the solid acid as  $48^\circ$ , whilst De Negri and Sburlati give it as  $43\cdot8^\circ$ ).

*Bromine Additive Product.*—Fifty grams of the crude acid were, according to Hazura's method (*Monatsh.*, 1887, **8**, 148), dissolved in 150 c.c. of glacial acetic acid, and to the solution, cooled by means of ice, 21 c.c. of bromine were gradually added with constant shaking; on thoroughly cooling the mixture, a crystalline precipitate separated out, together with some oily matter. After the precipitate had been repeatedly crystallised from glacial acetic acid and alcohol, its melting point was found to be  $114^{\circ}$ , which agrees with that of the bromine additive product of linolic acid,  $C_{18}H_{32}O_2$ . The bromine was estimated by Carius' method, with the following results:

I. 0.1830 gave 0.2279 AgBr. Br=53.01.

II. 0.2702 .. 0.3381 AgBr. Br=53.25.

$C_{18}H_{32}O_2Br_4$  requires 53.33; and  $C_{17}H_{30}O_2Br_4$ , 54.61 per cent.

On bromination, the pure recrystallised acid also gave a product melting at  $114^{\circ}$ , but its quantity was too small for a bromine estimation.

*Oxidation Products.*—30 grams of the crude acid were, again according to Hazura's method (*Monatsh.*, 1888, **9**, 198) mixed with 36 c.c. of caustic potash solution, sp. gr. 1.27, and the soap thus obtained was dissolved in 2 liters of water. To this solution were added, gradually and with constant shaking, 2 liters of 1.5 % potassium permanganate solution and, after standing for 12 hours, the precipitated manganese dioxide was filtered off. The filtrate, on acidifying with sulphuric acid, gave a white flocculent precipitate, which was separable into two acids by means of ether.

(1). A crude acid (about 5.3 % of the product of saponification), which was left behind after repeated extraction with ether and which, after purification by crystallisation, first from boiling water and then from alcohol, melted at  $171$ — $172^{\circ}$ ; determination of its neutralisation number led to the molecular weight 350.4 (sativic acid,  $C_{18}H_{32}(OH)_4O_2$



= 348, melting point  $173^{\circ}$ ). The results of its combustion were as follows :

0.1329 gave 0.3015  $\text{CO}_2$  and 0.1214  $\text{H}_2\text{O}$ .  $\text{C}=61.87$ ;  $\text{H}=10.16$ .

$\text{C}_{18}\text{H}_{32}(\text{OH})_4\text{O}_2$  requires  $\text{C}=62.07$ ;  $\text{H}=10.34$ .

(2). Another crude acid (yield one-fourth of the above acid) which, on evaporating the ethereal extract to a small bulk and cooling, was obtained in a crystalline state. After recrystallisation from alcohol it melted at  $126^{\circ}$ , and had the molecular weight 317.3 (dihydroxystearic acid,  $\text{C}_{18}\text{H}_{34}(\text{OH})_2\text{O}_2=316$ , melting point  $136^{\circ}$ ). Probably, therefore, this substance is impure dihydroxystearic acid.

No characteristic crystals of either linusic acid or isolinusic acid,  $\text{C}_{18}\text{H}_{30}(\text{OH})_6\text{O}_2$ , could be observed.

*Neutralisation number of the solid acid.*—The pure recrystallised solid acid (m.p.  $43-44$ ) from the oil was dried over sulphuric acid in an atmosphere of carbon dioxide; a weighed quantity was dissolved in neutralised alcohol and titrated with 0.0568-normal sodium hydroxide solution, using phenolphthalein as indicator. The molecular weight found were 280.6, 277.1, and 280.9. Titrations with standard barium hydroxide solution gave the numbers 283.1 and 280.7, the mean of all the determinations being 280.5, whilst  $\text{C}_{18}\text{H}_{32}\text{O}_2=280$ .

#### *Summary of the Results.*

1. The principal organic acids of the oil of *Elæococca vernicia* are a solid acid, m. p.  $43-44^{\circ}$ , and ordinary oleic acid, the former predominating.

2. The solid acid, which Cloëz named *elæomargaric acid*, and for which Maquenne recently proposed the name  *$\alpha$ -elæostearic acid*, has the composition  $\text{C}_{18}\text{H}_{32}\text{O}_2$ , and not  $\text{C}_{17}\text{H}_{32}\text{O}_2$ , as calculated by Cloëz, or  $\text{C}_{18}\text{H}_{30}\text{O}_2$ , as given by Maquenne.

3. The solid acid is, undoubtedly, a stereoisomeride of linolic acid, the bromine additive product,  $C_{18}H_{32}O_4Br_2$ , as well as the oxidation product,  $C_{18}H_{32}(OH)_2O_4$ , obtained from the former, agreeing in every respect with those obtained from the latter.



# Studien über die Reizwirkung einiger Metallsalze auf das Wachstum höherer Pflanzen.

von

Masayasu Kanda, *Rigakushi*.

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Mit 1 Tafel.

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## I. Einleitung und Litteratur.

In neuerer Zeit ist die Thatsache bekannt geworden, dass die Metallsalze im allgemeinen je nach ihren Konzentrationen verschiedenartige Einflüsse, d.h. das Wachstum beeinträchtigende oder fördernde Wirkung auf Pflanzenkörper ausüben. Abgesehen von den älteren Angaben haben die neueren und einige vor kurzem erschienene Arbeiten von RICHARDS,<sup>1)</sup> RUMM,<sup>2)</sup> HATTORI,<sup>3)</sup> ONO,<sup>4)</sup> LOEW,<sup>5)</sup> ASO<sup>6)</sup>

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1) H. M. RICHARDS: Die Beeinflussung des Wachstums einiger Pilze durch chemische Reize. Pringsh. Jarb. f. Wiss. Bot. Bd. XXX. 1897.

2) RUMM: Ueber die Wirkung der Kupferpräparate bei Bekämpfung der sogenannten Blattfallkrankheit der Weinreben. B.d. D.B.G. Bd. XI. 1893.

3) H. HATTORI: Studien über die Einwirkung des Kupfersulfats auf einige Pflanzen. Jour. Coll. Science, Imp. Univ. Tokyo. vol. XV. Pt. 3. 1901.

4) N. ŌNO: Ueber die Wachstumsbeschleunigung einiger Algen und Pilze durch chemische Reize. Jour. Coll. Science, Imp. Univ. Tokyo, vol. XIII, Pt. 1. 1900.

5) O. LOEW, K. ASO, & S. SAWA: Ueber die Wirkung von Manganverbindungen auf Pflanzen. Flora od. Allg. Bot. Zeit. 91 Bd. Ergänz. Bd. z. Jahrg. 1902.

6) K. ASO: On the Action of Sodium-Fluorid upon Plant life. Bull. Coll. Agr. Imp. Univ. vol. V. No. 2.

u.s.w.<sup>1)</sup> die Beweise erbracht, dass sowohl bei niederen als auch bei höheren Pflanzen das Wachsthum vegetativer Organe bedeutend beschleunigt wird, falls ihnen gewisse Metallsalze in geeigneten hoch verdünnten Konzentrationen geboten werden.

Indem ich hinsichtlich ausführlicher Angaben auf die betreffende Litteratur verweise, sei hier besonders hervorgehoben, dass die Resultate früherer Forscher nicht immer in allen Beziehungen übereinstimmend und sogar abweichend sind.<sup>2)</sup> Dies beruht zum Theil auf der Art und Weise der Versuchsanordnung, zum grossen Theile aber auf den Eigenschaften der angewandten Pflanzenobjecte, Eigenschaften, die in verschiedenen Arten, Spielarten, ja sogar je nach Individuen weit verschieden sein können. Ein grosser Fehler würde es sein, wenn man bei darartigen Studien eine nicht streng ausgewählte Pflanzensorte anwendet oder mit einer bestimmten Sorte in einer ungenügenden Anzahl experimentirt.

In der letzt erwähnten Beziehung bietet die Anwendung niederer Pflanzenobjecte vielfach Vorthail, da man vor allem eine grosse Anzahl von Individuen in relativ kleinen Räumen fortwachsen lassen kann, während es bei den höheren blühenden Pflanzen nicht der Fall ist. Es ist demgemäss wohl erklärlich, dass die bisherigen Versuche mit Phanerogamen nicht immer zu befriedigenden Ergebnissen geführt haben; in der That sind die Reaktionen bei höher organisirten Pflanzen viel verwickelter und vielseitiger als bei den niederen, einfacheren Formen.

Aus diesem Grunde würde es erwünscht sein, mit höheren Pflanzen eine Reihe ausgedehnter Versuche anzustellen, um die Koncentra-

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1) ADERHOLD: Ueber die Wirkungsweise der sogenannten Bordeaux-Brühe. *Centralb. f. Bakt. &c.* II. Abt. Bd. V. 1899. ANTON BAUMANN: Das Verhalten von Zinksalzen &c. *Landw. Vers. Stat.* Bd. XXXI. 1885.

2) Hierüber vergl. man: OTTO, R.: Ueber Aufnahme u. Speicherung &c. *Ref. Just, Bot. Jahrb.* Bd. XXI. I. 1893. P. 295., HASELHOFF: Ueber die schädliche Wirkung des Kupfersulfat &c. *Landw. Jahrb.* Bd. XXI. 1893., und H. HATTORI: l. c.

tionen zu finden, bei der die angewandten Metallsalze wachsthumfördernd einwirken könnten, und jene spezifische oder individuelle Verschiedenheit zu ermitteln, die unter Versuchspflanzen sicher existieren müssen.

Ich unternahm deshalb vorliegende Untersuchungen unter Anregung und Leitung von Herrn Prof. Dr. MIYOSHI, während eines akademischen Jahres, September 1902—Juni 1903, im botanischen Institute der Universität zu Tokio. Es sei mir gestattet Herrn Prof. Dr. MIYOSHI für seine vielseitige Anregung meinen verbindlichsten Dank auszusprechen.

## II. Methodisches.

Bei meinen Versuchen bediente ich mich folgender Metallsalze:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  und  $\text{NaF}$ , die alle aus der MERCK'schen Fabrik, als „garantiert reine“ Präparate stammten. Sie wurden hauptsächlich bei Wasser- und Topfkulturen verwendet. Als Versuchspflanzen wählte ich je eine bestimmte Sorte von *Pisum sativum*, var. *arvense* Poir., *Pisum arvense* L., und *Vicia Faba*, var. *equine* Pers., und *Fagopyrum esculentum* Mönch.

Die Samen von möglichst gleicher Grösse, wurden, nachdem sie etwa 24 Stunden unter Wasser getaucht und zum Aufquellen gebracht worden sind, in nassen Sägespänen ausgesaet. Die Keimlinge von einigen Centimetern Länge wurden, nach mehrmaligem Waschen mit destilliertem Wasser, zur Wasserkultur angewandt. Die Kulturgefässe hatten einen Inhalt von ca. 2 Litern, und waren mit von fünf Löchern durchzogenen Korkstöpseln versehen. Die Stöpsel wurden vorher mit Wasser andauernd gekocht, um dadurch etwaige lösliche Stoffe zu entfernen. Die Pflänzchen waren unter Zuhilfenahme von Watte durch die Löcher der Korken in die Lösungen gesteckt. Zum Waschen der Kulturgefässe benutzte ich zuerst konzentrierte Salzsäure,

dann wiederholt destilliertes Wasser; die äusseren Wände derselben wurden ferner mit schwarzem Papier bedeckt, um die Wurzeln der Pflänzchen vor dem Lichte zu schützen.

Als Kulturflüssigkeit bediente ich mich nur aus Glas destillierten Wassers, ohne Nährlösungszusatz, so dass die Ernährung der Keimlinge ausschliesslich von den Reservestoffen der Samen besorgt werden mussten. Dass ich dem Wasser keine Nährlösung zugab, hatte seinen Grund darin, dass der eine oder andere Stoff derselben zum Theil den Reizstoff ( $\text{CuSO}_4$  od.  $\text{ZnSO}_4$  etc.) fällt und somit die Wirkung des Letzteren aufheben kann. Um jene minimale Konzentration zu ermitteln, bei welcher das angewandte Metallsalz noch als Gift wirken kann, stellte ich zunächst eine Reihe von Wasserkulturen an mit Lösungen von verschiedener Stärke. Nach der Feststellung dieser Grenzkonzentration, wurden alle Lösungen von geringeren Konzentrationen zubereitet, welche für die nachstehenden Versuche dienen sollten. Die folgenden Zahlen geben die Konzentrationsgrade der Kulturlösungen.

#### Prozentgehalt an Kupfersulfat.

1.	$5 \times 10^{-8}$ Gr. Mol. in einem Liter.	=0. 000	00 1245 %
2.	$1 \times 10^{-8}$ „	=0. 000	000 2490 %
3.	$5 \times 10^{-9}$ „	=0. 000	000 1245 %
4.	$1 \times 10^{-9}$ „	=0. 000	0000 2490 %
5.	$5 \times 10^{-10}$ „	=0. 000	0000 1245 %
6.	$1 \times 10^{-10}$ „	=0. 000	00000 2490 %

#### Prozentgehalt an Zinksulfat.

1.	$1 \times 10^{-6}$ Gr. Mol. in einem Liter.	=0. 000	0 2870 %
2.	$5 \times 10^{-7}$ „	=0. 000	0 1435 %
3.	$1 \times 10^{-7}$ „	=0. 000	00 2870 %
4.	$5 \times 10^{-8}$ „	=0. 000	00 1435 %
5.	$1 \times 10^{-8}$ „	=0. 000	000 2870 %
6.	$5 \times 10^{-9}$ „	=0. 000	000 1435 %

## Prozentgehalt an Fluornatrium.

1.	$1 \times 10^{-3}$ Gr. Mol. in einem Liter.	=0. 00 42 %
2.	$5 \times 10^{-4}$ „	=0. 00 21 %
3.	$1 \times 10^{-4}$ „	=0. 000 42 %
4.	$5 \times 10^{-5}$ „	=0. 000 21 %
5.	$1 \times 10^{-5}$ „	=0. 0000 42 %
6.	$5 \times 10^{-6}$ „	=0. 0000 21 %

Die Versuche mit Topfpflanzen wurden in folgender Weise an- gestellt. Die Samen von *Fagopyrum*, *Pisum* und *Vicia* wurden in mit humoser Gartenerde gefüllten Töpfen von ca. 3 Litern Inhalt, aus- gesät. Diese Töpfe kamen an einen günstigen Ort, wo Licht, Wärme und andere äussere Faktoren möglichst gleichmässig blieben. Als die Sprossen drei bis vier Centimeter lang waren, wurden fünf von ihnen von möglichst gleicher Grösse und Gestalt in die Versuchstöpfe ge- pflanzt, und während einer bestimmten Zeitfrist mit 200 cc. Centimo- larelösungen der Salze begossen. Um die Feuchtigkeit in allen Töpfen möglichst gleich zu halten, erhielten die mit Metallsalzlösung nicht begossenen Töpfen gleichzeitig dieselbe Menge von Leitungswasser.

Wie bereits in der Einleitung betont wurde, existierten bei dem gleichartig aussehenden Samenmaterial einer und derselber Rasse, bedeutende individuelle Verschiedenheiten, die in Ausgestaltung und Wachstum jedes Keimlinges zum Vorschein kommen können. Unter Berücksichtigung dieses Punktes habe ich für Wasserkultur stets gleichaussehende zahlreiche Erbsenpflänzchen verwendet, um die in- dividuelle Differenz möglichst auszuschliessen.

Bei Fluorkulturen wandte ich, aus gewissen Gründen, stets in- wendig mit einem Firnis überzogene Glasgefässe an.

In keinem Falle, wurden bei den in destilliertem Wasser kulti-

vierten Erbsenpflanzen Wurzelknöllchen beobachtet. Die Lösungen wurden alle vier Tage erneuert.

### III. Das Verhalten einiger Kulturpflanzen in sehr verdünnten Kupfersulfat-, Zinksulfat- und Fluornatriumlösungen.

Bei dem Versuche mit *Pisum*keimlingen, kam aus Glasgefäßen destilliertes Wasser mit Zusatz von bestimmten Mengen der Metallsalze zur Verwendung, und die Zuwachsgrösse der Versuchspflanzen wurde nach einer bestimmten Zeitfrist in Bezug auf die Länge der Sprossen und der Wurzeln gemessen, ferner das Trockengewicht jedes Individuums ermittelt.

#### A. Kulturversuche mit $\text{CuSO}_4$ Lösungen.

Diese führten zum Resultate, dass die Kupfersulfatlösung auf Erbsenpflanzen, sogar bei einer Verdünnung von  $1 \times 10^{-8}$  Gr. Mol. d. h. 0.000 000 249 %, noch giftig ist, während noch verdünntere Lösungen z. B.  $1 \times 10^{-9}$  Gr. Mol. ( $=0.000\ 0000\ 249\ \%$ ) und  $1 \times 10^{-10}$  Gr. Mol. ( $=0.000\ 000\ 00\ 249\ \%$ ), weder als Gift noch als Beschleunigungsmittel einwirken.

Durch alle Versuchsreihen dieser Art, schienen die Kupfersulfatlösungen mit den Konzentrationen von  $1 \times 10^{-9}$  bis  $1 \times 10^{-10}$  Gr. Mol. zuweilen als wachstumsbeschleunigendes Mittel, mitunter aber einfach als Gift einzuwirken.<sup>1)</sup> Als Beispiele sei folgende zwei Fälle angegeben :

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1) Vergl. Tabelle I B, D & E und I; G, H & I.



(A).

*Pisum arvense* L.

	Konzentration der Lösungen von $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamte Trockengewicht der Sprosse und Wurzeln in Gr.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	9.1	—	.837	—
II.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249%.	8.2	— 0.9	.737	— .100
III.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245%.	8.5	— 0.6	.780	— .057
IV.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249%.	11.7	+ 2.6	.860	+ .023
V.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245%.	11.2	+ 2.1	.830	— .007
VI.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249%.	11.8	+ 2.7	.860	+ .023

(B).

*Pisum arvense* L.

	Konzentration der Lösungen von $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamte Trockengewicht der Sprosse und Wurzeln in Gr.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	15.0	—	.895	—
II.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1245%.	15.0	$\pm 0.0$	.874	— .021
III.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249%.	15.0	$\pm 0.0$	.962	— .033
IV.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245%.	14.0	— 1.0	.872	— .023
V.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249%.	13.0	— 2.0	.900	+ .005
VI.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245%.	12.8	— 2.2	.970	+ .075
VII.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249%.	14.0	— 1.0	.880	— .015

In (A) ist eine günstige Wirkung deutlich, in (B) aber ein schädlicher Einfluss unverkennbar. Durchschnittlich beobachtete ich, dass die in  $1 \times 10^{-8}$  Gr. Mol. Lösung verweilten Pflanzen immer schlechter vegetierten als die Kontrollpflanzen, wenngleich eine morphologische Veränderung bei den Versuchspflanzen sich nicht auffinden liess. Somit ist es zweifellos, dass die so stark verdünnte Kupfervitriollösung wie  $1 \times 10^{-8}$  Gr. Mol. für *Pisum*arten noch giftig wirkt. Andererseits sind aber die in weitaus verdünnten  $5 \times 10^{-9}$ — $1 \times 10^{-10}$  Gr. Mol. Lösungen nicht mehr sicher giftig und sogar indifferent. Selbstverständlich ist die Wirkungsweise je nach der individuellen Differenz des Versuchsobjectes verschieden.

## B. Kulturversuche mit $\text{ZnSO}_4$ Lösungen.

Diese ergaben, dass die minimale Grenzkonzentration für die Giftwirkung der Zinksulfatlösung auf *Pisum*keimlinge etwa bei  $5 \times 10^{-5}$  Gr. Mol. ( $=0.000\ 1435\%$ ) liegt. Versuche mit noch verdünnteren Lösungen führten mich zu nachstehenden Resultaten:

Spuren von Zinksulfat in Lösungen sind für einige Pflanzen absolut unschädlich, und können sogar das Wachstum der *Pisum*keimlinge beschleunigen, das optimale Konzentration liegt ungefähr zwischen  $1 \times 10^{-7}$  Gr. Mol. ( $=0.000\ 00\ 287\%$ ) und  $5 \times 10^{-9}$  Gr. Mol. ( $=0.000\ 000\ 1435\%$ ). Die wachsthumbeschleunigenden Wirkungen dieses Metallsalzes sind beispielweise aus folgender Tabelle zu sehen:

(C).

*Pisum arvense* L.

	Konzentration der Lösungen von $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .	Länge der Sprosse in Cm. mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse & Wurzeln in Gr.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	10.0	—	15.0	—	.956	—
II.	$1 \times 10^{-6}$ Gr. Mol. =0.000 0 287 %.	9.0	—1.0	15.0	$\pm 0.0$	.950	+ .006
III.	$5 \times 10^{-7}$ Gr. Mol. =0.000 0 1435 %.	9.0	—1.0	13.0	—2.0	.923	— .033
IV.	$1 \times 10^{-7}$ Gr. Mol. =0.000 00 287 %.	10.0	$\pm 0.0$	15.0	$\pm 0.0$	.930	— .026
V.	$5 \times 10^{-8}$ Gr. Mol. =0.000 00 1435 %.	11.5	+ 1.5	15.0	$\pm 0.0$	.990	+ .034
VI.	$1 \times 10^{-8}$ Gr. Mol. =0.000 000 287 %.	11.0	+ 1.0	16.5	+ 1.5	.957	+ .001
VII.	$5 \times 10^{-9}$ Gr. Mol. =0.000 000 1435 %.	10.8	+ 0.8	17.0	+ 2.0	.930	— .026

Bei  $1 \times 10^{-6}$  Gr. Mol. (=0.000 0 287 %) und  $5 \times 10^{-7}$  Gr. Mol. (=0.000 0 1435 %) Lösungen treten zuweilen abnormale Wuchsformen der Wurzeln auf, sonst sind die Pflanzen stets von geringeren Dimensionen als bei den Kontrollpflanzen. Zinksulfatlösungen im oben angegebenen Verdünnungsgrad sind deshalb auf einige Erbsenkeimlinge giftig.

Die wachstumbeschleunigende Wirkung des Zinksalzes auf Algen und Pilze wurde schon von Ōno nachgewiesen, auf Phanerogamen aber, so weit ich unterrichtet bin, ist bisher noch nicht konstatiert worden. Es ist mir deshalb vom gewissen Interesse die beschleunigende Wirkung der verdünnten Zinksulfatlösungen auf Blütenpflanzen hiermit zum ersten Male festgestellt zu haben.

### C. Kulturversuche mit NaF Lösungen.

Einige Vorversuche ergaben, dass bei *Pisum*keimlingen die Grenzkonzentration der NaF-Lösungen zwischen  $5 \times 10^{-3}$  Gr. Mol. oder 0.02 % bis  $1 \times 10^{-2}$  Gr. Mol. oder 0.04 % liegt. Danach bereitete ich einige verdünntere Lösungen, wie es schon im zweiten Kapitel angegeben wurde, und gelangte zu immer unzweideutigeren Resultaten, wie aus folgender Tabelle ersichtlich :

(D).

*Pisum arvense* L.

	Konzentration der Lösung von NaF.	Länge der Sprosse in Cm. mittel- aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen I.	Länge der Wurzeln in Cm. mittel- aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen I.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll I.
I.	Kontroll.	9.7	—	15.5	—	.888	—
II.	$1 \times 10^{-3}$ Gr. Mol. =0.00 42%.	9.1	—0.6	15.0	—0.5	.894	+ .006
III.	$5 \times 10^{-4}$ Gr. Mol. =0.00 21%.	15.2	+5.5	18.2	+2.7	.935	+ .047
IV.	$1 \times 10^{-4}$ Gr. Mol. =0.000 42%.	13.6	+3.9	17.5	+2.0	.840	— .048
V.	$5 \times 10^{-5}$ Gr. Mol. =0.000 21%.	15.7	+6.0	17.2	+1.7	.794	— .094
VI.	$1 \times 10^{-5}$ Gr. Mol. =0.000 0 42%.	9.7	$\pm 0.0$	15.3	—0.2	.880	— .008
VII.	$5 \times 10^{-6}$ Gr. Mol. =0.000 0 21%.	10.6	+0.9	15.0	—0.5	.870	— .018
VIII.	Kontroll.	10.6	+0.9	16.0	+0.5	.787	— .101

Aus obenstehender Tabelle wird ersichtlich, dass hoch verdünnte NaF-Lösungen auf die Erbsen-Pflanzen bedeutende wachstumsbeschleunigende Einwirkung ausüben, und ferner, dass die optimale Konzentration zwischen  $5 \times 10^{-4}$  Gr. Mol. oder 0.00 21 % und  $5 \times 10^{-5}$  Gr. Mol. oder 0.000 21 % liegt. Die in diesen Lösungen kultivierten

Pflanzen haben zahlreiche lange Seitenwurzeln hervorgetrieben, und die Sprosse wuchsen viel schneller als die in destilliertem Wasser kultivierten Kontrollpflanzen.

Wie Ōno<sup>1)</sup> und Aso<sup>2)</sup> bereits gezeigt haben, liegt der optimale Punkt der Reizwirkung des NaF für Algen etwa bei 0.000 0 3 %, und derselbe für die Gersten- und Reispflanzen etwa bei 0.00 5—0.00 1 % ; es geht daraus hervor, dass der Konzentrationsgrad des Fluornatriums, welcher den Erbsenpflanzen als ein Wachstumsbeschleunigungsmittel dient, höher ist als der für die Algen und niedriger als der für die Gersten- und Reispflanzen.

#### IV. Das Verhalten der Topfpflanzen gegen Kupfer- und Zinksulfatlösungen.

Bekanntlich werden manche Salzlösungen bei Berührung mit dem Boden nicht gleichmässig absorbiert ; bei andauernder Beriesung mit grossen Mengen von Lösung werden die Salze im Boden allmählich von oben nach unten fortschreiten ; diese eindringenden Salze werden von der Erde mehr oder weniger absorbiert, wodurch die Giftwirkung mancher Salze sehr erheblich vermindert werden kann.

Um die Frage, wie verhalten sich die Pflanzen, die in solchen entgiftend wirkenden Boden gepflanzt sind? zu beantworten, habe ich eine Reihe von Topfversuch (mit *Pisum*-, *Vicia*- und *Fagopyrum*-Pflanzen) mit Kupfer- und Zinksulfatlösung angestellt und gelangte zu folgenden Resultaten.

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1) N. Ōno: L. c. p. 165.

2) K. Aso: L. c.

Ogleich die mit ziemlich concentrirten Zink- oder Kupfer-Salzlösungen begossenen Topfpflanzen ihre Lebensthätigkeit lange Zeit beibehalten können, bei fortdauernden Berieselungen zeigen sie zuletzt die Symptome der Erkrankung und gehen zu Grunde. Wenn man sie jedoch mit hoch verdünnten Lösungen behandelt, ändern sich die Erscheinungen. Die Vegetationsverhältnisse der in dem humösen Boden wachsenden mit solchen Giftlösungen begossenen Pflanzen, sind nicht nur im geringsten nicht beschädigt, sondern gedeihen mehr oder weniger, wie die mit Leitungswasser begossenen Kontrollpflanzen.

#### A. Versuche mit Kupfersulfatlösung.

Ich beobachtete bei einigen Versuchen mit *Vicia* und *Pisum*, dass die Topfpflanzen, welche mit den mehr als Centimoral verdünnten Lösungen von Zeit zu Zeit gekupfert werden, nicht nur unvergiftet erscheinen, sondern im Gegentheil mehr oder weniger im ihren Wachsthum beschleunigt wurden. Beim mehrmaligen Begiessen mit Kupfersulfatlösung wird endlich eine grosse Menge Kupfersalzes in der Erde angehäuft werden, und müssen Giftwirkungen zu Tage treten. Ich beobachtete in zahlreichen Versuchen, wenn die gesammte Menge von  $\text{CuSO}_4$  etwa über 12 gr. gestiegen war, dass die Giftwirkung auf gewisse Pflanzenarten recht auffallend wurde; betrug die Kupfermenge etwa 5 bis 8 gr.  $\text{CuSO}_4$ , so wirkte das Metall vortheilhaft.

Folgende Tabelle zeigt die Resultate mit *Vicia Faba*:

(E).

*Vicia Faba L.*

	Zahl der Behandlungen pro Woche.	Totalsumma des festen Kupfersul- fates in Gram.	Zahl der neugebildete Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergli- chen mit Kontroll.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Totalsumma der Stämme und Wurzeln in Gram.
I.	Kontroll.	—	8.	41.8	—	6.7	6.0	12.7
II.	1 mal. pro Woche.	3.984	8.	49.7	+ 7.9	7.7	6.0	13.7
III.	2 mal. pro Woche.	5.976	8.	51.5	+ 9.7	9.1	5.5	14.6
IV.	Jeden Tag.	26.394	9.	54.5	+ 12.7	7.5	4.9	12.4

Bei Beendigung des Versuches, sahen die Blätter der oben bezeichneten Topfpflanzen IV. ziemlich gelb aus, die Wurzeln waren theilweise vergiftet, und eine Abnahme des Trockengewichtes resultierte. Die Versuche mit *Pisumpflanzen* verhielten sich ebenso, und zwar mit geringeren Schwankungen. *Flagopyrum esculentum* zeigte jedoch keine Veränderung bei der Berieselung, die dreimal pro Woche und im Ganzen 20 mal ausgeführt war; die totale Menge des  $\text{CuSO}_4$  betrug dabei 9.960 gr. Dennoch war eine starke Vergiftung der Stammtheile, die dicht oberhalb der Erdoberfläche lagen, sichtbar, als ich den Topf täglich mit  $\text{CuSO}_4$ -Lösung behandelte, bis die Totalmenge des Salzes auf 23.406 gr. gestiegen war.

In tabellarischen Zusammenstellungen stellte ich die Resultate der ganzen Versuchsreihe dar, die während einer langen Zeitfrist fort-dauerten, aber ich war schliesslich nicht im Stande, eine bestimmte Optimumkonzentration aufzufinden. Im Freien ist die Verdunstungsgrösse der Topferde von der Jahreszeit abhängig, und diese muss die Resultate der Topfversuche im hohem Grade beeinflussen. Diese störenden Einflüsse der Verdunstung können die Unbeständigkeit der Resultate in diesen Fällen verursacht haben, und in der That muss

der Einfluss der äusseren Faktoren grösser sein, als die beschleunigenden oder vergiftenden Wirkungen der Kupfersalze.

### B. Versuche mit Zinksulfatlösung.

Aus meinen Versuchsergebnissen geht deutlich hervor, dass die hoch verdünnten Zinksulfatlösungen, mit der die in Humusboden kultivierten Topfpflanzen behandelt wurden, auf das Wachstum der Pflanzen begünstigend einwirken können.

Ich beobachtete in einigen Versuchen mit *Pisum arvense* und *Vicia Faba*, dass Zinksulfat, das den Pflanzen als centimolare Lösung 3 mal pro Woche in Portionen von je 200 cc. zugesetzt war, (zwischen 5 und 13 gr. festes Zinksulfat) eine bedeutende Reizwirkung gezeigt hat, und ferner wenn die Menge etwa 25 gr. erreichte, die Gifterscheinung ziemlich bemerkbar wurde; jedoch zeigte in einem Falle, dass *Pisum arvense* sogar nach Behandlung mit 20.09 gr. nicht nur keine Schädigung, sondern eine normale Entwicklung erfuhr und somit keinen Unterschied von den Kontrollpflanzen zeigte.

Die folgende Tabelle zeigt ein Beispiel der Beobachtungen:

(F).

*Vicia Faba L.*

	Zahl der Behandlungen Pro Woche.	Totalsumma des festen Zinksulfats in Gram.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergli- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Totalsumma der Stämme und Wurzeln in Gram.
I.	Kontroll.	—	49.0	—	9.57	5.0	14.57
II.	Ein und nur I.	.574	47.0	—2.0	9.00	5.2	14.20
III.	1 mal. pro Woche.	1.722	49.5	+0.5	8.87	5.1	13.97
IV.	2 mal. pro Woche.	4.018	53.0	+4.0	9.95	5.1	15.05
V.	3 mal. pro Woche.	5.740	56.5	+8.5	10.90	5.2	16.10



*Eragopyrum esculentum* zeigte keinen Unterschied von den Kontrollpflanzen nach dreimaliger Berieselung pro Woche (Summa 9.758 gr.) ; doch durch tägliche Berieselung (Summa 22.96 gr.), ähnlich bei  $\text{CuSO}_4$ -Versuchen, wurden die Stämme, die der Erde näher lagen, stark vergiftet.

BAUMANN<sup>1)</sup> hat bereits in seiner Arbeit über die Einwirkung des Zinksalzes betont, dass Zinkvitriol in dem einem Boden schädliche Wirkungen hervorbringen mag, während in einem anderen Boden durch Begiessen mit derselben Lösung für die Vegetation günstige Erscheinungen beobachtet werden können. Auch in meinen Versuchen beobachtete ich, dass Humuserde aus dem Garten dieses Institut eine Beschleunigungserscheinung zeigte, sie wird daher der letzteren Erdsorte BAUMANN's ähnlich sein. In unseren Fällen wirkte Zinksulfat, welches als Centimolarelösung bei den Topfpflanzen in Anwendung kam, nie als Gift, bis die gesammte Menge festen Salzes etwa 15 gr. erreichte, die optimale Dosis für Wachsthumbeschleunigung liegt etwa bei 5-12 gr.

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Die Reizwirkung der Metallsalze in Topfversuchen, insbesondere beim Kupfersalz, konnte ich leider nicht immer mit genügender Sicherheit konstatieren. Um diese Misserfolge aufzuklären, müssen folgende Umstände in Betracht gezogen werden.

- 1). Die chemische Wechselwirkung eines Metallsalzes mit den komplexen Verbindungen im Humusboden.
- 2). Die Ungleichheit des Wachstums der Kontrollpflanzen, die in verschiedenen Töpfen gezogen wurden, war sehr erheblich,

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1) ANTON BAUMANN. Das Verhalten von Zinksalzen gegen Pflanzen und im Boden. Landw. vers. Stat. Bd. XXXI. 1885.

obzwar die Pflanzen in einem und demselben Topfe ziemlich gleichmässig vegetierten.

Der Einfluss der Jahreszeiten, and zwar der der Temperatur- und Feuchtigkeitsveränderungen, scheint die Einwirkungen der Metallsalze in hohem Grade zu modificieren. Ich beobachtete, dass in kalter aber feuchter Zeit, infolge der Transpirationsverminderung die Giftwirkung der Metallsalze bedeutend verringert wurde, obwohl sie reichlich in der Erde vorhanden waren, während in warmer und trockner Saison, wegen zu starker Verdunstung die Giftwirkung sehr erhöht war. Diese und noch andere meteorologische sowie klimatologische Factoren verursachen hier in der That sehr verschiedene Effekte.

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Ausser oben erwähnten Versuchen, führte ich unter andersartigen Versuchsanordnungen noch folgende vier Experimente aus, die ich hier kurz erwähne: Erstens, die Blätter der Topfpflanzen wurden mit hoch verdünnten Metallsalzlösungen bespritzt; zweitens, dieselbe Lösung wurde mittelst einer PRAVATZschen Spritze in die Gefässtheil der weichen Topfpflanzen (*Vicia*, *Pisum* u. Kartoffelpflanzen) hineingespritzt; drittens, liess ich nach der Methode, die HANSTEEN<sup>1)</sup> in seiner Arbeit über Eiweissynthese angewandt hat, die verdünnten Lösungen direkt die Cambiumschichte berühren, und von dort aus einsaugen; viertens, es kam das Aetherverfahren nach der Methode JOHANSEN's<sup>2)</sup> zur Anwendung.

Fast alle diese Versuche ergaben aber keine nennenswerthe Resultate. Im ersten Falle, wurde wegen der Verdunnung der

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1) BARTHOLOM HANSTEIN, Ueber Eiweissynthese in grünen Phanerogamen. Jahrb. f. W. Bot. Bd. 33. 1899.

2) W. JOHANSEN. Das Aether-Verfahren beim Frühtreiben mit besonderer Berücksichtigung der Fließtreiberei. 1900.

bespritzten Lösung die Konzentration so gesteigert, dass die Blätter schliesslich zu Grund gingen; im zweiten Falle, trat infolge des Zerreissens des Gewebekomplexes oft das Welken des darüberliegenden Theils ein; und im dritten starb das Cambium ehe die Lösung genügend eingesaugt worden war. Nur im vierten Falle, beobachtete ich, dass das Blühen des Kirschbäume, welche als Versuchsobjekt angewandt waren, nach 24 stündigen Aetherisieren mit 20 cc. Aether pro Heetliter Luft, im Vergleiche mit Kontrollpflanzen früher eintrat.

## V. Schlussbemerkungen und Zusammenfassung der Resultate.

Aus den vorstehenden Untersuchungen geht zunächst hervor, dass einige Pflanzen in ihrem Gedeihen durch eine geringe Zugabe von gewissen Metallsalzen, welche für sich nicht als Nährstoffe, sondern in grösseren Dosen als Gift einwirken, günstig beeinflusst werden. Von den geprüften Metallsalzen konnte ich nur bei Kupfersulfat bei den Wasserkulturen von meinen Versuchspflanzen (Erbsen) die besprochene Reaktion nicht konstatiren. Bei meinen Versuchen wirkte das Kupfersalz in so starker Verdünnung, wie 0.000 000 2 %, entschieden noch als Gift, und bei Anwendung der weiter verdünnten Lösungen war eine wachsthumsbeschleunigende Einwirkung nicht nachweisbar.

Von den von mir angewandten Versuchsmethoden haben nur Wasser- und Topfkultur brauchbare Resultate geliefert während alle anderen (vergl.: p. 16-17) für unseren Zweck sich nicht besonders geeignet erwiesen.

Wasser- und Topfkultur haben beide ihren Vor- und Nachtheil. Bei der ersteren kann man einen Stoff in reinem Zustande oder auf direktem Wege einwirken lassen, obgleich das Kultiviren einer Landpflanze im Wasser sie in abnormalen Zustand

versetzt, während bei der letzteren d.h. Topfkultur, welche die Pflanze möglichst im natürlichen Zustande belässt, man dies keineswegs erwarten kann, da das Absorptionsvermögen des Bodens für Gifte das Resultat sehr modificirt, was bei Verschiedenheit der Böden wohl berücksichtigt werden muss.

Die wesentlichsten Resultate können folgendermassen zusammengefasst werden:—

1. Stark verdünnte Kupfersulfatlösung kann schon bei 0.000 000 249% auf *Pisum*keimlinge in Wasserkultur schädlich einwirken, und noch weiter verdünnte von 0.000 000 0 249—0.000 000 00 249 % wirken weder als Gift noch als Reizmittel. Aber in gewissen Böden kann  $\text{CuSO}_4$  als Reizmittel wirken: Die mit 200 cc. von 0.249 %  $\text{CuSO}_4$  Lösung zweimal pro Woche begossenen *Pisum* und *Vicia* Topfpflanzen zeigen stärkeres Gedeihen nach 5 bis 8 Wochen, d.h. bei 10-14 maligen Berieselungen mit ca. 5-7 gr. des festen Kupfersulfats.

2. Das Gedeihen der *Pisum*keimlinge in Wasserkultur wird durch Zugabe von Zinksulfat im höchst verdünnten Zustande begünstigt, die optimale Konzentration liegt zwischen 0.000 00 287% und 0.000 000 1435%; bei einer Konzentration 0.000 0 287 % wirkt sie bereits als Gift. Die mit 200 cc. von 0.287 %  $\text{ZnSO}_4$  dreimal pro Woche begossenen *Vicia* und *Pisum* Topfpflanzen zeigen ein schnelleres Wachstum als die mit Leitungswasser begossenen Kontrollpflanzen im Verlauf der 3 bis 6 Wochen, d.h. bei 10-20 maligen Berieselungen, in welchen die totale Menge von  $\text{ZnSO}_4$  ca. 5—13 gr. beträgt.

3. Fluornatrium-Lösung kann für das Wachstum der *Pisum*keimlinge in Wasserkultur als Reizmittel dienen; die optimale Konzentration liegt zwischen 0.00 21 % und 0.000 21 %. Sie wirkt bei 0.02 % schon als Gift.

## Tabellarische Zusammenstellung.

I. Wasserkultur von Erbsenkeimlingen mit Zusatz von  
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

Tab. A.

*Pisum sativum*, var. *arvense* POIR.,—angestellt 25 Sept. 1902.

Kulturdauer 23 Tage.

Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	15.2	—	1.165	—
II.	$1 \times 10^{-8}$ Gr. Mol. =0.000 000 249%.	14.5	−0.7	1.117	−.048
III.	$5 \times 10^{-9}$ Gr. Mol. =0.000 000 1245%.	15.8	+0.6	1.167	+ .002
IV.	$1 \times 10^{-9}$ Gr. Mol. =0.000 000 0 249%.	15.2	$\pm 0.0$	1.137	−.028
V.	$5 \times 10^{-10}$ Gr. Mol. =0.000 000 0 1245%.	13.6	−1.6	1.105	−.060
VI.	$1 \times 10^{-10}$ Gr. Mol. =0.000 000 00 249%.	10.6	−4.6	0.990	−.175

Tab. B.

*Pisum sativum*, var. *arvense* POIR.,—angestellt 29 Oct. 1902.

Kulturdauer 18 Tage.

Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	6.0	—	1.275	—
II.	$1 \times 10^{-8}$ Gr. Mol. =0.000 000 249%.	7.5	+1.5	1.157	−.118
III.	$5 \times 10^{-9}$ Gr. Mol. =0.000 000 1245%.	6.9	+0.9	1.132	−.143
IV.	$1 \times 10^{-9}$ Gr. Mol. =0.000 000 0 249%.	6.0	$\pm 0.0$	1.234	−.041
V.	$5 \times 10^{-10}$ Gr. Mol. =0.000 000 0 1245%.	6.9	+0.9	1.339	+ .064
VI.	$1 \times 10^{-10}$ Gr. Mol. =0.000 000 00 249%.	4.5	−1.5	1.132	−.143

Tab. C.

*Pisum arvense* L.,—————angestellt 30 Oct. 1902.

Kulturdauer 18 Tage.

Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	8.2	—	1.126	—
II.	$5 \times 10^{-8}$ Gr. Mol. =0.000 00 1245%.	6.6	—1.6	1.002	— .124
III.	$1 \times 10^{-8}$ Gr. Mol. =0.000 000 249%.	6.6	—1.6	0.961	— .165
IV.	$5 \times 10^{-9}$ Gr. Mol. =0.000 000 1245%.	10.0	+1.8	1.137	+ .011
V.	$5 \times 10^{-10}$ Gr. Mol. =0.000 000 0 1245%.	9.1	+0.9	1.270	+ .144

Tab. D.

*Pisum arvense* L.,—————angestellt 17 Nov. 1902.

Kulturdauer 10 Tage.

Temperatur 15°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	9.1	—	.837	—
II.	$1 \times 10^{-8}$ Gr. Mol. =0.000 000 249%.	8.2	—0.9	.737	— .100
III.	$5 \times 10^{-9}$ Gr. Mol. =0.000 000 1245%.	8.5	—0.6	.780	— .057
IV.	$1 \times 10^{-9}$ Gr. Mol. =0.000 000 0 249%.	11.7	+2.6	.860	+ .023
V.	$5 \times 10^{-10}$ Gr. Mol. =0.000 000 0 1245%.	11.2	+2.1	.830	— .007
VI.	$1 \times 10^{-10}$ Gr. Mol. =0.000 000 00 249%.	11.8	+2.7	.860	+ .023

Tab. E.

*Pisum arvense* L., ————— angestellt 4 Febr. 1903.

Kulturdauer 20 Tage.

Temperatur 12°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	10.0	—	0.947	—
II.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1245 %.	9.1	—0.9	0.966	+ .019
III.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249 %.	10.6	+0.6	0.932	— .015
IV.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245 %.	10.0	$\pm 0.0$	0.995	+ .048
V.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249 %.	10.6	+0.6	1.051	+ .104
VI.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245 %.	9.7	—0.3	0.978	+ .031
VII.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249 %.	9.0	—1.0	0.861	— .086

Tab. F.

*Pisum arvense* L., ————— angestellt 25 Febr. 1903.

Kulturdauer 23 Tage.

Temperatur 12°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	15.0	—	0.895	—
II.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249 %.	15.0	$\pm 0.0$	0.862	— .033
III.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245 %.	14.0	—1.0	0.872	— .023
IV.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249 %.	13.0	—2.0	0.900	+ .005
V.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245 %.	12.8	—2.2	0.970	+ .075
VI.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249 %.	14.0	—1.0	0.880	— .015

Tab. G.

*Pisum arvense* L., ————— angestellt 14 März, 1903.

Kulturdauer 20 Tage.

Temperatur 12°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamntes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	15.0	—	1.030	—
II.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249 %.	12.0	—3.0	0.940	— .090
III.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245 %.	12.—15.	—3. bis $\pm 0$ .	0.987	— .043
IV.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249 %.	11.5	—1.5	0.857	— .173
V.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245 %.	13.0	—2.0	1.037	+ .007
VI.	Kontroll.	12.0	—3.0	0.957	— .073

Tab. H.

*Pisum arvense* L., ————— angestellt 17 Apr. 1903.

Kulturdauer 15 Tage.

Temperatur 12°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamntes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	9.0	—	0.840	—
II.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249 %.	8.5	—0.5	0.815	— .025
III.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245 %.	8.3	—0.7	0.942	+ .102
IV.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249 %.	8.2	—0.8	0.980	+ .140
V.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245 %.	9.0	$\pm 0.0$	0.807	— .033
VI.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249 %.	8.0	—1.0	0.977	+ .137



Tab. I.

*Pisum arvense* L., ————— angestellt 17 Apr. 1903.  
Kulturdauer 20 Tage. Temperatur 12°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	16.0	—	0.850	—
II.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1245 %.	14.5	—1.5	0.880	+ .030
III.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249 %.	10.5	—5.5	0.832	— .018
IV.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245 %.	13.0	—3.0	0.802	— .048
V.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249 %.	12.5	—3.5	0.815	— .035
VI.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245 %.	12.0	—4.0	0.937	+ .087
VII.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249 %.	14.0	—2.0	0.917	+ .067
VIII.	Kontroll.	15.5	—0.5	0.949	+ .099

Tab. J.

*Pisum arvense* L., ————— angestellt 2 Mai, 1903.  
Kulturdauer 15 Tage. Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	10.5	—	1.077	—
II.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1245 %.	8.5	—2.0	1.017	— .060
III.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 249 %.	10.0	—0.5	1.057	— .020
IV.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1245 %.	9.0	—1.5	1.046	— .031
V.	$1 \times 10^{-9}$ Gr. Mol. = 0.000 000 0 249 %.	10.5	±0.0	1.021	— .056
VI.	$5 \times 10^{-10}$ Gr. Mol. = 0.000 000 0 1245 %.	10.0	—0.5	1.029	— .048
VII.	$1 \times 10^{-10}$ Gr. Mol. = 0.000 000 00 249 %.	11.0	+0.5	1.032	— .045
VIII.	Kontroll.	10.2	—0.3	1.015	— .062

II. Wasserkultur von Erbsenkeimlingen, mit Zusatz  
von  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .

Tab. A.

*Pisum arvense* L., ————— angestellt 13 Nov. 1902.

Kulturdauer 15 Tage.

Temperatur  $15^\circ - 20^\circ\text{C}$ .

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	13.5	—	0.835	—
II.	$5 \times 10^{-7}$ Gr. Mol. = 0.000 0 1435%.	12.1	—1.4	0.827	—0.008
III.	$1 \times 10^{-7}$ Gr. Mol. = 0.000 00 287%.	14.0	+0.5	0.845	+0.010
IV.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1435%.	14.0	+0.5	0.810	—0.025
V.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 287%.	18.0	+4.5	0.827	—0.008

Tab. B.

*Pisum arvense* L., ————— angestellt 25 Nov. 1902.

Kulturdauer 14 Tage.

Temperatur  $12^\circ - 20^\circ\text{C}$ .

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	8.5	—	14.5	—	1.030	—
II.	$1 \times 10^{-6}$ Gr. Mol = 0.000 0 287%.	8.0	—0.5	15.0	+0.5	1.025	—0.005
III.	$5 \times 10^{-7}$ Gr. Mol. = 0.000 0 1435%.	8.5	$\pm 0.0$	15.0	+0.5	0.951	—0.079
IV.	$1 \times 10^{-7}$ Gr. Mol. = 0.000 00 287%.	8.5	$\pm 0.0$	15.0	+0.5	1.047	+0.017
V.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1435%.	9.5	+1.0	15.5	+1.0	1.172	+0.142
VI.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 287%.	8.7	+0.2	17.0	+2.5	1.035	+0.005
VII.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1435%.	8.8	+0.3	15.0	+0.5	1.050	+0.020

Tab. C.

*Pisum arvense* L., ————— angestellt 21 Febr. 1903.

Kulturdauer 16 Tage.

Temperatur 12° — 20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längendifferenz der Sprosse in Cm. verglichen mit Kontrollpflanzen.	Gesamtes Trockengewicht der Sprosse und Wurzeln in Gram.	Trockengewicht- differenz in Gr. verglichen mit Kontrollpflanzen.
I.	Kontroll.	8.0	—	0.887	—
II.	$1 \times 10^{-6}$ Gr. Mol. = 0.000 0 287%.	8.0	$\pm 0.0$	0.731	— .156
III.	$5 \times 10^{-7}$ Gr. Mol. = 0.000 0 1435%.	8.0	$\pm 0.0$	0.805	— .082
IV.	$1 \times 10^{-7}$ Gr. Mol. = 0.000 00 287%.	8.4	+ 0.4	0.850	— .037
V.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1435%.	8.4	+ 0.4	0.920	+ .033
VI.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 287%.	8.6	+ 0.6	0.855	— .032

Tab. D.

*Pisum arvense* L., ————— angestellt 12 Apr. 1903.

Kulturdauer 14 Tage.

Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	10.0	—	15.0	—	0.956	—
II.	$1 \times 10^{-6}$ Gr. Mol. = 0.000 0 287%.	9.0	— 1.0	15.0	$\pm 0.0$	0.950	+ .006
III.	$5 \times 10^{-7}$ Gr. Mol. = 0.000 0 1435%.	9.0	— 1.0	13.0	— 2.0	0.923	— .033
IV.	$1 \times 10^{-7}$ Gr. Mol. = 0.000 00 287%.	10.0	$\pm 0.0$	15.0	$\pm 0.0$	0.930	— .026
V.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1435%.	11.5	+ 1.5	15.0	$\pm 0.0$	0.990	+ .034
VI.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 287%.	11.0	+ 1.0	16.5	+ 1.5	0.957	+ .001
VII.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1435%.	10.8	+ 0.8	17.0	+ 2.0	0.930	— .026

Tab. E.

*Pisum arvense* L., ————— angestellt 12 Mai, 1903.  
Kulturdauer 15 Tage. Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	12.5	—	17.0	—	0.962	—
II.	$1 \times 10^{-6}$ Gr. Mol. = 0.000 0 287 %.	9.5	—3.0	15.5	—1.5	0.987	+ .025
III.	$5 \times 10^{-7}$ Gr. Mol. = 0.000 0 1435 %.	13.5	+1.0	18.0	+1.0	0.840	— .122
IV.	$1 \times 10^{-7}$ Gr. Mol. = 0.000 00 287 %.	12.5	$\pm 0.0$	17.5	+0.5	0.982	+ .020
V.	$5 \times 10^{-8}$ Gr. Mol. = 0.000 00 1435 %.	14.5	+2.0	18.0	+1.0	0.931	— .031
VI.	$1 \times 10^{-8}$ Gr. Mol. = 0.000 000 287 %.	12.3	—0.2	16.0	—1.0	0.950	— .012
VII.	$5 \times 10^{-9}$ Gr. Mol. = 0.000 000 1435 %.	15.5	+3.0	18.0	+1.0	0.940	— .022

III. Wasserkultur von Erbsenkeimlingen, mit Zusatz  
von NaF.

Tab. A.

*Pisum arvense* L., ————— angestellt 30 Okt. 1902.

Kulturdauer 20 Tage.

Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gramm.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	9.7	—	15.5	—	0.888	—
II.	$1 \times 10^{-3}$ Gr. Mol. = 0.00 42 %.	9.1	— 0.6	15.0	— 0.5	0.894	+ .006
III.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21 %.	15.2	+ 5.5	18.2	+ 2.7	0.935	+ .047
IV.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42 %.	13.6	+ 3.9	17.5	+ 2.0	0.840	— .048
V.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21 %.	15.7	+ 6.0	17.2	+ 1.7	0.794	— .094
VI.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42 %.	9.7	$\pm 0.0$	15.3	— 0.2	0.880	— .008
VII.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21 %.	10.6	+ 0.9	15.0	— 0.5	0.870	— .018
VIII.	Kontroll.	10.6	+ 0.9	16.0	+ 0.5	0.787	— .101

Tab. B.

*Pisum arvense* L., ————— angestellt 23 Nov. 1902.

Kulturdauer 16 Tage.

Temperatur 15°—20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gramm.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	9.1	—	18.2	—	0.775	—
II.	$1 \times 10^{-3}$ Gr. Mol. = 0.00 42 %.	7.6	— 1.5	10.0	— 8.2	0.706	— .069
III.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21 %.	10.0	+ 0.9	15.2	— 3.0	0.825	+ .050
IV.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42 %.	9.1	$\pm 0.0$	15.1	— 3.1	0.852	+ .077
V.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21 %.	14.0	+ 4.9	16.4	— 1.8	0.725	— .050
VI.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42 %.	9.1	$\pm 0.0$	16.0	— 2.2	0.792	+ .017
VII.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21 %.	8.5	— 0.6	13.3	— 4.9	0.770	— .005

Tab. C.

*Pisum arvense* L., ————— angestellt 9 Dec. 1902.  
Kulturdauer 14 Tage. Temperatur 15°–20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	9.1	—	18.2	—	0.857	—
II.	$1 \times 10^{-3}$ Gr. Mol. = 0.00 42 %.	10.0	+ 0.9	18.2	$\pm 0.0$	0.985	+ 0.128
III.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21 %.	11.4	+ 2.3	20.0	+ 1.8	0.940	+ 0.083
IV.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42 %.	11.4	+ 2.3	18.7	+ 0.5	0.879	+ 0.022
V.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21 %.	10.6	+ 1.5	25.0	+ 6.8	1.005	+ 0.148
VI.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42 %.	10.0	+ 0.9	17.5	— 0.7	0.840	— 0.017
VII.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21 %.	10.0	+ 0.9	17.5	— 0.7	0.926	+ 0.069

Tab. D.

*Pisum arvense* L., ————— angestellt 11 Febr. 1903.  
Kulturdauer 16 Tage. Temperatur 12°–20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	9.8	—	18.5	—	1.045	—
II.	$1 \times 10^{-3}$ Gr. Mol. = 0.00 42 %.	9.1	— 0.7	12.4	— 6.1	1.092	+ .047
III.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21 %.	10.0	+ 0 2	16.4	— 2.1	1.025	— .020
IV.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42 %.	13.0	+ 3.2	18.5	$\pm 0.0$	1.135	+ .090
V.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21 %.	9.7	— 0.1	15.4	— 3.1	0.890	— .155
VI.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42 %.	9.5	— 0.3	15.9	— 2.6	0.960	— .085
VII.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21 %.	9.1	— 0.7	18.2	— 0.3	0.954	— .091

Tab. E.

*Pisum arvense* L., ————— angestellt 3 März, 1903.  
Kulturdauer 20 Tage. Temperatur 12°–20°C.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	13.0	—	18.	—	0.924	—
II.	$1 \times 10^{-3}$ Gr. Mol. = 0.00 42%.	9.5	–3.5	13.	–5.	0.923	–.001
III.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21%.	12.0	–1.0	16.	–1.	0.929	+ .005
IV.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42%.	13.5	+0.5	18.	±0.	0.961	+ .037
V.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21%.	12.0	–1.0	16.	–2.	0.903	–.021
VI.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42%.	10.0	–3.0	15.	–3	0.962	+ .038
VII.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21%.	12.0	–1.0	16.	–2.	0.862	–.062

Tab. F.

*Pisum arvense* L., ————— angestellt 24 Apr. 1903.  
Kulturdauer 13 Tage. Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	8.0	—	15.	—	0.942	—
II.	$1 \times 10^{-3}$ Gr. Mol. = 0.00 42%.	8.0	±0.0	12.	–3.	0.972	+ .030
III.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21%.	13.0	+5.0	14.	–1.	1.285	+ .343
IV.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42%.	11.0	+3.0	16.	+1.	1.095	+ .153
V.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21%.	8.5	+0.5	16.	+1.	1.090	+ .148
VI.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42%.	10.0	+2.0	16.	+1.	1.090	+ .148
VII.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21%.	13.0	–5.0	18.	+3.	1.135	+ .193

## Tab. G.

*Pisum arvense* L., ————— angestellt 7 Mai, 1903.

Kulturdauer 14 Tage.

Zimmertemperatur.

	Konzentration der Lösungen.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Sprosse in Cm. vergli- chen mit Kontroll- pflanzen.	Länge der Wurzeln in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz der Wurzeln in Cm. vergli- chen mit Kontroll- pflanzen.	Gesamtes Trocken- gewicht der Sprosse und Wurzeln in Gram.	Trocken- gewicht- differenz in Gr. vergli- chen mit Kontroll- pflanzen.
I.	Kontroll.	8.5	—	18.2	—	0.943	—
II.	$5 \times 10^{-4}$ Gr. Mol. = 0.00 21%.	10.5	+2.0	19.0	+0.8	1.010	+ .067
III.	$1 \times 10^{-4}$ Gr. Mol. = 0.000 42%.	10.2	+1.7	17.5	—0.7	1.065	+ .122
IV.	$5 \times 10^{-5}$ Gr. Mol. = 0.000 21%.	9.5	+1.0	18.2	$\pm 0.0$	1.020	+ .077
V.	$1 \times 10^{-5}$ Gr. Mol. = 0.000 0 42%.	9.5	+1.0	16.0	—2.2	0.881	— .062
VI.	$5 \times 10^{-6}$ Gr. Mol. = 0.000 0 21%.	9.7	+1.2	17.0	—1.2	0.991	+ .048



## IV. Topfkultur mit Behandlung mit Kupfersulfatlösungen.

Tab. A.

*Vicia Faba*, var. *equine* PERS.,—angestellt 29 Sept. 1902.

Kulturdauer 70 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Kupfer- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. verglie- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	8.	41.8	—	6.7	6.0	12.7
II.	1 mal pro Woche.	3.984	8.	49.7	+ 7.9	7.7	6.0	13.7
III.	2 mal pro Woche.	5.976	8.	51.5	+ 9.7	9.1	5.5	14.6
IV.	Jeden Tag.	26.394	9.	54.5	+12.7	7.5	4.9	12.4

die Blätter IV<sup>te</sup> Pflanzen ziemlich gelb gefärbt.

Tab. B.

*Pisum sativum*, var. *arvense* POIR.,—angestellt 29 Sept. 1902.

Kulturdauer 70 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Kupfer- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. verglie- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	2.	56.4	—	7.80	2.240	10.040
II.	1 mal pro Woche.	3.984	3.	53.9	—2.5	8.80	2.155	10.955
III.	2 mal pro Woche.	5.976	2.	61.8	+5.4	9.99	1.850	11.840
IV.	3 mal pro Woche.	10.956	1.	53.0	—3.4	8.00	2.030	10.030
V.	Jeden Tag.	26.394	1.	50.9	—5.5	7.60	2.375	9.975

Tab. C.

*Vicia Faba*, var. *equine* PERS.,—angestellt 13 Okt. 1902.

Kulturdauer 80 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Kupfer- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergl. chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	9.	43.9	—	8.60	6.30	14.9
II.	Ein und nur Ein.	.498	9.	46.6	+ 2.7	9.20	7.00	16.2
III.	1 mal pro Woche.	4.482	6.	41.8	— 2.1	7.70	4.85	12.5
IV.	2 mal pro Woche.	8.466	7.	48.5	+ 4.6	9.10	7.90	17.0
V.	3 mal pro Woche.	12.450	8.	55.1	+11.2	10.40	6.50	16.9
VI.	Jeden Tag.	28.884	5.	45.5	+ 1.6	8.00	4.60	12.6

Tab. D.

*Pisum arvense* L.,—angestellt 14 Nov. 1902.

Kulturdauer 112 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Kupfer- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergl. chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	0.	?	?	15.5	7.90	23.40
II.	Ein und nur Ein.	.498	1.	„	„	21.2	7.02	28.22
III.	1 mal pro Woche.	5.478	0.	„	„	19.5	8.20	27.70
IV.	2 mal pro Woche.	10.459	1.	„	„	19.5	7.42	26.92
V.	3 mal pro Woche.	15.936	4.	„	„	20.0	7.90	27.90
VI.	Jeden Tag.	27.390	1.	„	„	19.5	7.00	26.50

Tab. E.

*Vicia Faba*, var. *equine* Pers.,—angestellt 22 Febr. 1903.

Kulturdauer 70 Tage.

Im Freien.

Zahl der Behandlungen Pro Woche.		Total- summa des festen Kupfer- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. verglie- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	5.	36.2	—	12.5	6.00	18.50
II.	Ein und nur Ein.	.498	7.	34.5	-1.7	10.1	5.45	15.55
III.	1 mal pro Woche.	3.984	7.	36.4	+0.2	13.2	5.85	19.05
IV.	2 mal pro Woche.	7.968	6.	39.2	+3.0	12.2	7.85	20.05
V.	3 mal pro Woche.	11.952	5.	36.5	+0.3	13.1	6.00	19.10
VI.	3 mal pro Woche.	11.952	9.	36.5	+0.3	14.9	7.50	22.40

Tab. F.

*Vicia Faba*, var. *equine* Pers.,—angestellt 19 Apr. 1903.

Kulturdauer 45 Tage.

Im Freien.

Zahl der Behandlungen Pro Woche.		Total- summa des festen Kupfer- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. verglie- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	0.	46.	—	13.80	6.70	20.5
II.	Ein und nur Ein.	.498	0.	46.	±0.	13.20	6.70	19.9
III.	1 mal pro Woche.	1.992	0.	47.	+1.	13.50	6.10	19.6
IV.	2 mal pro Woche.	4.482	0.	47.	+1.	13.00	6.20	19.2
V.	3 mal pro Woche.	6.474	0.	48.	+2.	15.20	6.80	22.0

## V. Topfkultur mit Behandlung mit Zinksulfatlösungen.

Tab. A.

*Pisum arvense* L.,—angestellt 29 Sept. 1902.

Kulturdauer 70 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergl. chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	0.	110.6	—	4.0	0.915	4.915
II.	1 mal pro Woche.	4.592	0.	118.2	+7.6	4.1	0.715	4.815
III.	2 mal pro Woche.	8.610	0.	112.1	+1.5	4.7	1.065	5.765
IV.	3 mal pro Woche.	13.202	0.	115.1	+4.5	5.5	0.555	6.055
V.	Jeden Tag.	33.866	0.	106.1	-4.5	3.2	0.695	3.895

Tab. B.

*Vicia Faba*, var. *equine* Pers.,—angestellt 28 Okt. 1902.

Kulturdauer 65 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergl. chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	6.	36.3	—	11.5	10.0	21.5
II.	Ein und nur Ein.	5.74	8.	36.8	+0.5	13.7	12.2	25.9
III.	1 mal pro Woche.	5.166	9.	33.3	-3.0	13.5	13.0	26.5
IV.	2 mal pro Woche.	9.758	6.	39.0	+2.7	14.0	13.0	27.0
V.	3 mal pro Woche.	14.350	6.	39.4	+3.1	15.5	13.0	28.5
VI.	Kontroll.	—	5.	38.4	+2.1	10.0	12.0	22.0

Tab. C.

*Vicia Faba*, var. *equine* PERS.,—angestellt 7 Nov. 1902.

Kulturdauer 110 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergli- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	5.	?	?	17.0	15.0	32.0
II.	Ein und nur Ein.	.574	8.	„	„	14.2	13.0	27.2
III.	1 mal pro Woche.	6.888	6.	„	„	17.7	14.5	32.2
IV.	2 mal pro Woche.	13.202	8.	„	„	17.6	15.0	32.6
V.	3 mal pro Woche.	20.096	5.	„	„	17.0	13.8	30.8

Tab. D.

*Vicia Faba*, var. *equine* PERS.,—angestellt 22 Febr. 1903.

Kulturdauer 70 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergli- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	8.	35.2	—	10.9	4.75	15.65
II.	Ein und nur Ein.	.574	6.	38.1	+2.9	10.9	4.33	15.23
III.	1 mal pro Woche.	4.592	10.	35.0	—0.2	11.1	4.77	15.87
IV.	2 mal pro Woche.	9.184	7.	34.8	—0.4	10.6	4.38	14.98
V.	3 mal pro Woche.	13.776	8.	40.0	+4.8	12.1	4.27	16.37
VI.	3 mal pro Woche.	13.776	8.	40.8	+5.6	13.7	4.95	18.65

Tab. E.

*Vicia Faba*, var. *equine* PERS.,—angestellt 19 Apr. 1903.

Kulturdauer 40 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergl.- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht- der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	1.	49.0	—	9.57	5.0	14.57
II.	Ein und nur Ein.	.574	0.	47.0	—2.0	9.00	5.2	14.20
III.	1 mal pro Woche.	1.722	0.	49.5	+0.5	8.87	5.1	13.97
IV.	2 mal pro Woche.	4.018	0.	53.0	+4.0	9.95	5.1	15.05
V.	3 mal pro Woche.	5.740	0.	56.5	+8.5	10.90	5.2	16.10

Tab. F.

*Vicia Faba*, var. *equine* PERS.,—angestellt 13 Mai, 1903.

Kulturdauer 35 Tage.

Im Freien.

	Zahl der Behandlungen Pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in Cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergl.- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u. Wurzeln in Gram.
I.	Kontroll.	—	0.	34.	—	6.52	6.0	12.52
II.	1 mal pro Woche.	2.296	0.	47.	+13.	8.54	6.2	14.74
III.	2 mal pro Woche.	4.018	0.	48.	+14.	8.53	5.9	14.43
IV.	3 mal pro Woche.	5.740	0.	45.	+12.	8.49	5.6	14.09

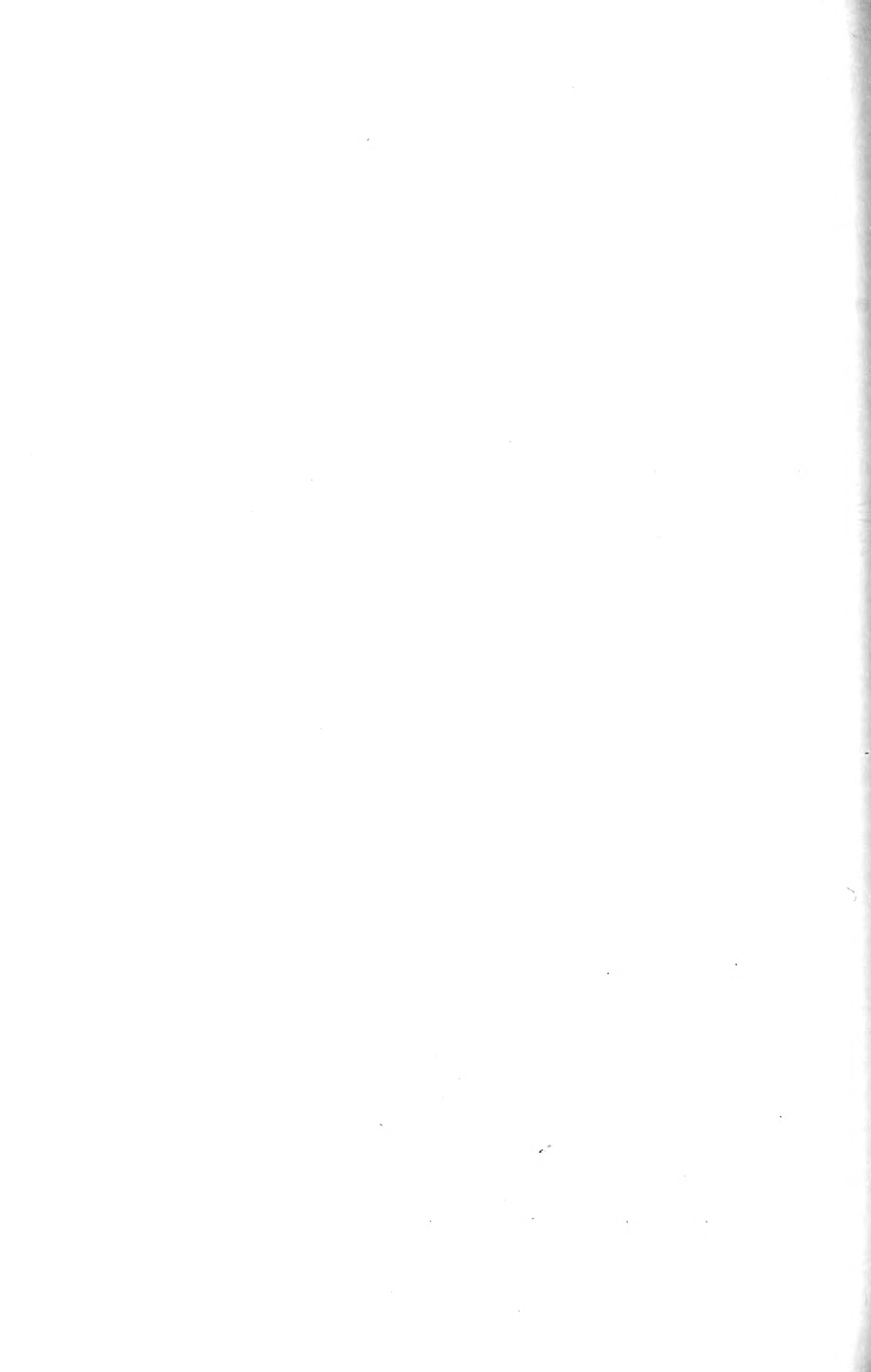
Tab. G.

*Vicia Faba*, var. *equine* PERS.,—angestellt 13 Mai, 1903.

Kulturdauer 35 Tage.

Im Freien.

	Zahl der Behandlungen pro Woche.	Total- summa des festen Zink- sulfates in Gram.	Zahl der neugebil- deten Stämme.	Länge der Sprosse in cm. Mittel aus je 5 Pflanzen.	Längen- differenz in Cm. vergli- chen mit Kontroll- pflanzen.	Trocken- gewicht der Stämme in Gram.	Trocken- gewicht der Wurzeln in Gram.	Total Trocken- gewicht der Stämme u Wurzeln in Gram.
I.	Kontroll.	—	0.	44.	—	8.52	6.7	15.22
II.	1 mal pro Woche.	2.296	0.	47.	+ 3.	8.54	6.7	15.24
III.	2 mal pro Woche.	4.018	0.	49.	+ 5.	8.54	6.4	14.94
IV.	3 mal pro Woche.	5.740	3.	47.	+ 3.	8.52	5.0	13.52





## Inhalt.

- I. Einleitung und Litteratur.
- II. Methodisches.
- III. Das Verhalten einiger Kulturpflanzen in sehr verdünnten Kupfersulfat-, Zinksulfat- und Fluornatriumlösungen.
- IV. Das Verhalten der Topfpflanzen gegen Kupfer- und Zinksulfatlösungen.
- V. Schlussbemerkungen und Zusammenfassung der Resultate.

## Tabellarische Zusammenstellung.

- I. Wasserkultur von Erbsekeimlingen, mit Zusatz von  $\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$ .
  - II. „ „ „ „ „ „ „  $\text{Zn SO}_4 \cdot 7\text{H}_2\text{O}$ .
  - III. „ „ „ „ „ „ „  $\text{NaF}$ .
  - IV. Topfkultur mit Behandlung mit Kupfersulfatlösungen.
  - V. „ „ „ „ „ Zinksulfatlösungen.
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TAFEL.

### Erklärung der Fig. I.

Wasserkulturen von *Pisum arvense* L. mit und ohne Zusatz von NaF.  
(Photographiert am 18ten Tage nach der Versuchsanstellung).

Ohne Zusatz ; Kontrollkultur.

I.	Mit Zusatz von 0. 000	42 %
II.	Mit Zusatz von 0 00	21 %
III.	Mit Zusatz von 0. 000	42 %
IV.	Mit Zusatz von 0. 000	21 %
V	Mit Zusatz von 0. 000 0	42 %
VI.	Mit Zusatz von 0. 000 0	21 %

Ohne Zusatz ; Kontrollkultur.

### Erklärung der Fig. II.

Topfversuche von *Vicia Faba*, var. *equine* PERS. mit und ohne Behandlung mit  $\text{Cu SO}_4$  lösungen

(Photographiert nach der Beendigung der Versuche)

I. Berieselung nur mit Leitungswasser ; Kontrollkultur

II. Berieselung mit 200 cc. Centimolarelösung von  $\text{CuSO}_4$  1 mal pro Woche ;  
Totalsumma des festen  $\text{CuSO}_4$  betrug 3.984 gr.

III. Berieselung mit 200 cc. Centimolarelösung von  $\text{CuSO}_4$  2 mal pro Woche ;  
Totalsumma des festen  $\text{CuSO}_4$  betrug 5.976 gr.

IV. Berieselung mit 200 cc. Centimolarelösung von  $\text{CuSO}_4$  Täglich ; Totalsumma  
der festen  $\text{Cu SO}_4$  betrug 26.394 gr ; die Blätter dieser Pflanzen sind ziemlich gelb gefärbt.

### Erklärung der Fig. III.

Topfversuche von *Vicia Faba*, var. *equine* PERS. mit und ohne Berieselung mit  $\text{Zn SO}_4$  lösungen.

(Photographiert nach Beendigung der Versuche).

I. Berieselung nur mit Leitungswasser ; Kontrollkultur.

II. Berieselung mit 200 cc. Centimolarelösung von  $\text{ZnSO}_4$  1 mal pro Woche ;  
Totalsumma des festen  $\text{ZnSO}_4$  betrug 2.296 gr.

III. Berieselung mit 200 cc. Centimolarelösungen von  $\text{ZnSO}_4$  2 mal pro Woche ;  
otalsumma des festen  $\text{ZnSO}_4$  betrug 4.018 gr.

IV. Berieselung mit 200 cc. Centimolarelösungen von  $\text{ZnSO}_4$  3 mal pro Woche ;  
Totalsumma des festen  $\text{ZnSO}_4$  betrug 5.740 gr.

Fig. I.



Fig. II.



Fig. III.



Autor Photo.

M. KANDA: Reizwirkung einiger Metallsalze auf das Wachstum höherer Pflanzen.



A

Study of the Genicula of Corallinæ.

By

K. Yendo, *Rigakushi*.

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*With one Plate.*

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INTRODUCTION.

The genicula of the *Corallinæ* are of special interest from both morphological and physiological point of view. The presence or the absence of a geniculum in Corallinaceous algae forms the essential character on which is based the division of the family into two subfamilies, viz., the *Corallinæ* and the *Melobesinæ*.

In certain other calcareous algae, such as *Galaxaura*, *Actinotrichia*, *Halimeda*, *Cymopolia*, &c., we also find genicula of a similar appearance. Although these genera are systematically apart from one another, there can be no doubt that the physiological function of genicula is the same in all cases.

A comparative study of the genicula in all these members would surely afford us interesting results. In the present paper, however, the observation is confined to the *Corallinæ*.

As far as the present writer's observation extends, the literature relating to the subject in question is comparatively scarce. NELSON and DUNCAN<sup>1)</sup> jointly tried some investigations into the histology of

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1) On Some Points in the Histology of Certain Species of Corallinaceæ.

the calcareous algæ, and left a valuable paper. SOLMS<sup>1)</sup> treated somewhat the same subject, and wrote a few lines about the formation of the genicula in the *Corallina*; and pointed out the difference between *Amphiroa* and *Corallina* in the structure of genicula. HEYDRICH<sup>2)</sup> noticed the critical points of the primary incrustation of *Corallina* and *Lithothamnion*. He took *Corallina officinalis*, L. as the representative of the *Corallina* and mentioned the genicular formation as an important diverging point of the two subfamilies.

The writer previously noticed several interesting facts about the genicula of the *Corallina*, while he was examining material from Japan and Canada. Some of the views arrived at a different conclusion from those of former investigators. They will be pointed out under the proper chapters.

The material worked over belongs mostly to the Japanese and the Canadian algæ. They were preserved in alcohol directly after they had been collected or after decalcifying the fresh plants in PERÉNY's fluid. The specimens which were kindly sent to the writer by Dr. M. FOSLIE, Madame A. WEBER VAN BOSSE, Mr. F. S. COLLINS, Major THEO. REINHOLD were a great help to him in comparing results. The writer must not miss the chance to express his deepest thanks to these phycologists. Thanks are also due to Prof. J. MATSUMURA, Prof. M. MIYOSHI and others who have helped the writer in various ways.

The writer regrets to say that the study on *Amphiroa stelligera* and *Amphiroa aspergillum*, which play an important and interesting part in the present work, he has been obliged to undertake on dried material. He could not help omitting several important observations on these species, as, with dried fronds, he was unable to pursue the

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1) GRAF v. SOLMS-LAUBACH. *Corallina* p. 28.

2) *Lithothamnion* von Helgoland. p. 72.



course further. Moreover specimens of *Amphiroa australis* were not accessible to him. This is the only species which is reported to have the fronds constructed with globular cells. The writer does not doubt that minute study on the structure of this species might afford interesting facts to add to the present work.

Botanical Institute,

Imperial University of Tokyo.

October, 1903.

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### EXTERNAL APPEARANCE OF GENICULA.

The genicula of *Coralline* appear with a brownish colour while the plant is yet living. In some of the members which have no significant genicula, the colour is, as a consequence, not remarkable. When the fronds are bleached and the articuli have turned into chalky white, the genicula are distinguishable as yellowish brown constrictions or rings around the calcareous fronds.

The genicula are entirely free from the deposit of calcium, and the substance is horny and flexible. This gives a special character to the fronds. Whether a frond is robust or not depends essentially upon the relative size of the genicula and the accompanying articuli. Even in an individual the proportion differs in the basal and the upper parts of the frond.

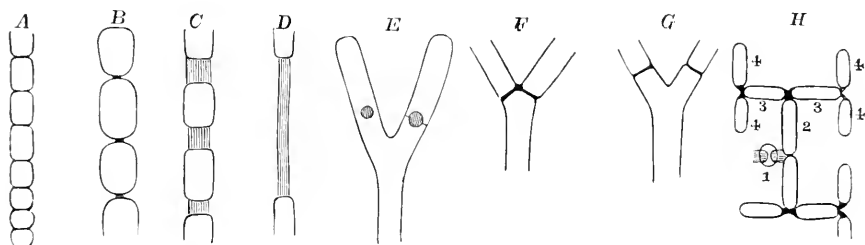
The majority of *Coralline* have very short genicula at the basal part of the frond. The articuli at this region are mostly short and cylindrical. Hence the stem at this part becomes moniliform, the genicula taking the places of the constrictions. *Amphiroa dilatata*, *Amp. Bowerbankii*, *Amp. canaliculata*, *Amp. ephedraea*, etc., in short, those which would be grouped under the section *Eurytion*, Dene., have the genicula with equal or nearly equal diameter with the articuli adjacent.

The genicula of *Amp. stelligera*, *Amp. Charoides* and their allied forms are the larger than those of the other species. Some of the matured genicula, indeed, are longer than the accompanying articuli. They are cylindrical, smaller in diameter than the articuli.

When the fronds of the *Coralline* are observed with the naked eye, we can easily distinguish several forms of the genicula. These multitudinous shapes might be classified briefly into the following five types :

I. *Linear*: the majority of *Corallina*, *Jania* and some of *Amphiroa* belong to this type. As for the basal genicula, most of the members come under this category. The exceptions are the greater number of the *Eurytion*, *Amp. Charoides*, *Amp. stelligera* etc., and many species of *Cheilosporum* (Fig. A).

The gap between the articuli is very narrow, apparently seen only as a circumscribing slit around the geniculum. This sort of genicula has been called "lineæform" by the former systematists. In these the genicula are not so short as they appear from the external side. Both ends of the articuli which hold the geniculum between them are concave. Hence the greater part of the geniculum is covered by the overhanging margins of the relating articuli. I shall call this marginal portion, for sake of convenience, the circum-genicular cortex (Pl. fig. 1-2).



The genicula of *Amp. aspergillum*, when judged by the external appearance, come under this category. But the internal structure of the frond in this species is quite different from that of the other members of the *Corallinæ*. As it will be treated further in the following pages, we can not clearly distinguish the genicular and the articular portions in its internal structure.

II. *Spotty*: many of the section *Arthrocardia*, Dene. belong to this type, especially those which have the sagittate articuli ending in narrow base. (fig. B).

In these the diameter of the geniculum is much smaller than that of the adjacent articuli; and the greater part of the geniculum is exposed outside. Or, in other words, the part exposed to the outside is comparatively larger than the part hidden under the circumgenicular cortex. Hence the genicula of this type appear to the naked eye like brownish spots.

III. *Bandform*: the genicula at the lower portions of the members under the section *Eurytion*, *Dene*, belong to this type (fig. E).

This type of genicula has the diameter equal or nearly equal to that of the adjacent articuli. The length is comparatively great. The articuli are destitute of circumgenicular cortex. On the contrary, a portion of the distal end of an articulus is covered by the outgrowth of the successive geniculum. The details will be given in a later chapter.

IV. *Filiiform*: the peculiar genicula of *Amp. stelligera*, *Amp. Charoides*, etc., belong to this type (fig. D).

They are very long genicula, often several times longer than the diameter. The diameter of the genicula is smaller than that of the articuli, hence the whole appearance is filiform. In the youngest stage of its development it is undistinguishable from "spotty" genicula as in the upper parts of *Amp. canaliculata*.

V. *Fenestraform*: the genicula at the upper portions of the fronds of *Amp. dilatata*, *Amp. ephedraea*, *Amp. Bowerbankii*, etc., belong to this type.

The genicula here mentioned are by no means the complete ones. They are always to be found at the upper and younger portions of the fronds which are without exception furnished with the "bandform" genicula at the basal parts. The "fenestraform" genicula, therefore, should be taken only as a young stage of the "bandform"

type. Yet the genicula of the present type characterise a species in a great degree. It would be better, therefore, to mention them on the same level with the other forms (fig. E).

The above mentioned five types are easily discernible with the naked eye. The divergency of the genicula into these types is due to the difference of the modes in the early stage of their development. Some minute account of the histological views will be given in the following chapters.

### THE POSITION OF GENICULA.

The embryonal stage of the *Corallinæ* is a mere thin calcareous incrustation upon a substratum. In this stage it is not easily distinguished from a sterile form of some *Melobesia*. The tiny epiphytic species, such as *Corallina pusilla* and *Cor. radiata* have their basal incrustation in the shape of a verruculose circular disc.

Every member of the *Corallinæ*, however, soon develops a mammillary process perpendicular to the surface of the incrustation. The process becomes provided with an uncalcified joint, the primary or the basal geniculum, slightly above the level of the surface of the incrustations. cf. HEYDRICH'S paper on "*Lithothamnion von Helgoland*."<sup>1)</sup> The mammillary process continues to grow upward acropetally, having the geniculum at fixed distances. The intergenicular portions are so-called articulari.

The intergenicular distance or the height of an articularis is always comparatively short at the basal part of a frond. As the plant grows larger, the successive upper articulari become larger and larger, sometimes compressed simultaneously, inclining to its proper shape in each species. This circumstance is nearly similar in every member except tiny and epiphytic forms.

When the articuli at the basal portion grow in thickness, after they have been geniculated, the consequence is that they always assume a moniliform shape: and if the growth of the diameter of the genicula has corresponded to that of the articuli, we have a homogeneous cylinder with parallel rings at certain distances. In the former case the result is always "linear" in form, as in *Amp. aberrans*, *Cor. officinalis* and many others: in the latter case "bandform" genicula are formed, as in *Amp. dilatata*, *Amp. ephedrea*, &c.

At the upper portions of the fronds we find several differences in the position of the genicula. These various positions may be divided into two, the normal and the abnormal.

#### A. THE NORMAL POSITION.

The normal position of genicula is always at the ends of the articuli, situated in the direction of the rachis. This position is most common in the members of the *Corallinæ*. And the genicula belonging to the axial stem or to the main branches are of this type.

There might be two equal or several unequal genicula at the distal end of an articulus. In the former case the two genicula are mostly separated in the meridional plane. This results in the branching mode which I have called the "direct" dichotomy<sup>1)</sup> (fig. F). In some dichotomous fronds, a single geniculum is on the top of each arm of Y-shaped articuli, instead of two genicula at the diverging point, forming the branching mode which I have called "indirect" dichotomy (fig. G). In *Cor. decussato-dichotoma* and its allied species, the two genicula are situated, side by side, at the top of an articulus. But the partition plane of both genicula is always

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1) YENDO: *Cor. verae Japon.* p. 10. footnote.

at right angles to that of the next order. The consequence is that the dichotomy of one order comes in the plane at right angles to that of the adjacent one. This mode of dichotomy is what I called "decussato-dichotomy." (fig. II).

A peculiar mode of bifurcation is found in the main stems of *Amp. aspergillum*. In this species the articuli of the main stems are as broad as their length and strongly compressed except those at the basal portion. A few of the successive articuli below a bifurcating articulus are much more complanated and have a longitudinal groove along the meridional line, as if the tendency of the bifurcation at the upper articulus were already indicated in the lower articuli.

When several unequal genicula have been formed at the distal end of an articulus, the branching mode becomes much more complex. In the pinnated fronds, the two minor genicula are on both sides of the middle one; and when several minor ones are around the axial one, the mode is whorly. In either case the middle and large one is situated in the direction of the rachis and is always at the center of the distal area.

Strictly speaking, the size and the position of the genicula at the distal end of an articulus from which the trichotomy and the pinnation begin are different. In the trichotomy three genicula, equal in size and in value, start at the end of an articulus from the same level. In the pinnated branchlets, the two genicula on both sides of the axial geniculum are much smaller than the latter. The genicular cells of the axial one start from the zone lower by one than that of the genicular cells of the pinnules (fig. 3). This was actually observed in *Amp. aberrans*, *Cor. officinalis*, *Cheilosporum maximum*, etc. (cf. fig. 11, Plate 1. *Cor. veræ Japon.*).

The genicular cells have no power to develop into articular cells by division or elongation. They are always transformed from the

cells of a certain portion of an articulus. The difference of the level from which the genicula start illustrates the fact that they are of separate origin. Hence at least in the last mentioned species the genicula of the ramuli or the pinnules are not genetically related to those of the neighbouring axial articulus. It should be admitted that the pinniferous articulus might be taken conveniently as a sagittated one with the shoulders enormously prolonged and finally jointed.

*Amp. stelligera* and *Amp. Charoides*, as well as their allied forms, have a peculiar mode of ramification. This has been already remarked by KÜTZING in his *Tab. Phyc.* vol. VIII. p. 26. The branches never start like all other members of the *Coralline* directly from an articulus. The primary geniculum of a ramus or ramulet always starts from a certain limited part of the axial geniculum, and not from an articulus. The whorly branchlets of these species, therefore, have quite a distinct morphological significance from those of *Cor. pilulifera*, *Cor. rancouveriensis*, etc. which are mentioned below. Hence in the former species the branchlets are practically developed at the expense of the axial geniculum. I was not able satisfactorily to trace the origin of the branchlets, as the material would not allow me to do so ; but it was clearly observed that the embryonal stage of the branchlets is readily recognizable around the immature axial geniculum. How the genicula could give out branchlets will be noticed hereafter.

The genicula of the pinnated and the whorly fronds are always at certain angles to one another. The angles between the genicula of the axis and the pinnules are geometrically adjacent angles to the angle formed by the axial articulus and the pinnules. Here the angle between the genicula means that which has been formed by the planes perpendicular to the periclinal axes of the axial articulus and the pinnules concerned.



The extreme case of pinnation is that of *Amp. aspergillum*. The more or less compressed articuli of the main stem are regularly jointed at certain distances. The genicula are linear, with subequal diameter to the articuli. The primary articulus of the branchlets arise decussately from the upper end of the periclinal edge of the compressed articulus. The insertion of the pinnæ or the primary genicula is at right angles to the axial geniculum.

As the position of genicula is dependent upon the mode of branching, the plants with irregular branching have naturally the genicula at indefinite positions. The larger number of the section *Euamphiroa*, Denc. are examples of this category.

In *Amp. valonioides* a branch often arises obliquely upwards from the distal end of an axial articulus with its primary geniculum at some distance further than the diverging point. This gives an appearance of sympodium until we examine the internal structure. cf. *Cor. veræ Japon.* Pl. I. fig. 3.

*Amp. cretacea* has an irregular mode of branching. It sometimes gives out branches at the distal end of an articulus showing apparant dichotomy. On the other side, several branches arise decussately from the periclinal side of a cylindrical articulus. The latter is by no means the abnormal but a special mode of ramification belonging to this species. cf. Pl. IV. fig. 2. l. c.

These decussate branches have the primary geniculum in two forms. The first is that of the geniculum directly situated upon the surface of the axial articulus ; that is, the geniculum starting without any process on the surface of the articulus. The second form has the genicula upon the process, perpendicular or obliquely, produced on the surface. These modes of geniculation might correspond to "direct" and "indirect" dichotomy. But the character is not

constant in equal degree as in the case of dichotomy ; and both types may be found in the same individual. cf. Pl. IV. fig. 2. l. c.

Some of the plants which belong to the section *Eucorallina*, and might be classified near *Cor. officinalis*, have often numerous genicula around the axial one. The writer has mentioned actual examples in *Cor. pilulifera* and *Cor. vancouveriensis*, *f. densa*.<sup>1)</sup> The subordinate genicula belong mostly to the stalks of the conceptacles. Although this arrangement of conceptacles characterises the plant in some measure, in considering the position of the genicula, the whorly genicula in this species would better be treated as of less importance. It should not be forgotten, however, that the origin of these whorly genicula is entirely different from those of *Amp. stelligera*, etc.

#### B. ABNORMAL POSITION.

As has been already remarked in the preceeding chapter, every geniculum accompanies an articulus, whether it be of branch, pinnule or stem. Hence the abnormal position of a geniculum means a geniculum belonging to an abnormal branch or branchlet. The most common case of such abnormality is found on the flat surface or margin of an articulus. Illustrious examples have been given in *Amp. aberrans*<sup>2)</sup> and *Amp. canaliculata*.<sup>3)</sup> In these species the branchlets consisting of one or more articuli originate on the surface or the margins of the articuli. In most cases the form of branches and the shape of the articuli of these abnormal ramules are much modified. To give the minor points of these modifications is, at present, not necessary. These abnormal branches have the genicula directly on the surface of the articuli. Very often, in the case of *Amp. aberrans*,

1). *Cor. verae* of Port Renfrew. Pl. I, VI. fig. 17 : *Cor. verae* Japon. Pl. III. fig. 16.

2). *Cor. verae* Japon. Pl. II. fig. 1-2.

3). **Martens**: Preus. Exp. nach Ostas. Tange. Pl. VI.

a knotty protuberance is found at the point of insertion of the geniculum into the articulus. In *Amp. canaliculata*, Mart. the genicula are always directly attached to the margins of the articulus, that is to say, the genicula grow from the margins without any protuberance or prolongation of the calcified portion.

In most cases the abnormal genicula seem to have generated from the cortex. In *Amp. cretacea*, a number of the cortical cells increase layer upon layer at a certain portion of the surface of an articulus in such a degree as to produce a wart-like protuberance. One of the cellular layers elongates to an extraordinary degree, in like manner as a normal genicular formation, and thus the primary geniculum is built up.

Some of the branches of *Amp. cretacea*, *Amp. valonioides*, etc. originate from the cortex in the manner just described above. In *Amp. aspergillum* the primary genicula of the pinnules are always generated from the cortex. These ramules are by no means abnormal branches in these species, but a characteristic mode of ramification limited to them.

Thus the genicula at the distal end of an articulus which give rise to dichotomy, trichotomy, whorly or pinnation (not of *Amp. aspergillum*) are originated from the medulla; and those of the lateral branches or processes are mostly from the cortex. The abnormal genicula generally belong to the latter category.

#### RELATIVE POSITION OF THE GENICULAR AND THE ARTICULAR CELLS.

The structure of the articuli of the *Corallinæ* may be easily divided into two portions. The internal part is constructed with long filamentous cells bound together along the periclinal side of the cells. These cells occupy the greater part of the diameter. The cells at the

middle portion run in the direction of the axis of the articulus. Those at the peripheral portion more and more become inclined, diminishing, at the same time, in the length, until they result in globular or cubical cells running radially to form the cortex. The medullary cells are mostly arranged in zones. These zones are easily observable when the calcium carbonate in the frond has been dissolved. They appear as concentric parallel lines, convex toward the apex of the frond (figg. 3, 5, 6).

A geniculum is built up with one or more zones of the periclinal cells. The majority of the *Coralline* belong to the former category. In the case when one zone of the periclinal cells shared the formation of geniculum, the middle portions of the cells serve as the geniculum proper. Both ends of the cells have the deposit of calcium carbonate and have no proper function as genicular cells. The calcified distal ends should for the sake of convenience be called the extra-genicular portion (figg. 9-10).

The bordering line between the articuli and both ends of a geniculum varies more or less according to the species. As has been mentioned above, a geniculum is not built up by the mass of the entire cell but by a mass of parts of the cells. In other words, the cells at the critical portion which divide a geniculum and an articulus are separated into two parts, the one serving to build the geniculum and the other the articulus (figg. 1, 2, 4). Hence the word "borders" does not apply to the continuation of the cell boundaries. It means the continuity of the transitional points of the genicular and the articular portions of the cells; or the critical points of the genicular and the extragenicular portions.

In the hair-like *Jania* the number of the genicular cells is much less than that of the robust forms, and they are arranged in a less regular manner. Generally speaking, the cells at the middle portion

of a geniculum are longer than those in the periphery. But there occurs much fluctuation in the length, and the longitudinal section of a geniculum always shows a zigzag appearance, cf. *Cor. veræ Japon.* Pl. III. fig. 3.

In *Amp. aberrans* the genicular area changes abruptly into the articular portion, and the boundaries between them are exceedingly sharp. The boundaries are more or less convex toward the articular parts at both ends of the geniculum. The majority of the *Corallinæ* are of this respect, although the sharpness of the boundaries may fluctuate in a slight degree (fig. 3).

*Amp. dilatata*, which shows special characters in various points, here also gives us an aberrant type in this respect. The upper boundary is a concave plane running into the geniculum and the lower is a convex one running toward the lower articulus, with special outgrowth at the central portion of both planes (fig. 5). This character, however, is limited to the genicula of the upper and middle portions of the fronds. The genicular cells of this plant undergo further development and an old geniculum has an appearance quite foreign to that of the younger ones.

In *Cheilosporum anceps*, the zonal arrangement of the periclinal cells is entirely disturbed. The cells are not straight but undulating, and are connected with one another through the large lateral openings (fig. 4). In this respect it resembles the cellular arrangement of the *Jania*, especially *Cor. yenoshimensis*, cf. *Cor. veræ Japon.* Pl. III. fig. 3.

Although the zonal arrangement of the periclinal cells is thus irregular, the transition parts are regularly and sharply defined (fig. 4).

In *Cor. decussato-dichotoma* and *Cor. yenoshimensis* the periclinal cells are not undulated as in *Cheil. anceps* but the perforation on the

lateral walls and the non-zonal arrangement of the cells are similar to those of the latter species.

The above mentioned genicula are all those in the normal position. The characters are more or less constant to the species. In the abnormal genicula, as it were, these descriptions may not be often sharply applied.

The greater part of this chapter does not hold good in the fronds of *Amp. aspergillum*. In this species an articulus is built up of two and only two zones of the periclinal cells, covered with a few layers of cortical cells. The lower of the two zones practically fills up the entire portion of the medulla. The cells constructing it are much-elongated filaments of nearly equal length, running longitudinally in an exact sense. The upper zone is a layer of elliptical cells, each of which is situated at the top of the filamentous cell. These elliptical cells have their longer axis in the same direction as the filamentous cells below them, but those at the peripheral region bend horizontally by degrees and finally become confluent with the cells of the innermost cortical layer. Hence in the longitudinal sections of an articulus we have a  $\cap$ -shaped layer of minute cells holding the bundle of the filamentous cells wholly inside of it. The boundary of the neighbouring articuli lies at the points where the basal extremities of the filamentous cells of an articulus come into contact with the terminal extremities of the elliptical cells of the lower articulus. The slit between the articuli which suggests a linear geniculum in the external appearance of a frond, is around this region (fig. 7).

We have several reasons for believing that the lower half of the filamentous cells serves as the genicular portion proper of the other species. In the preparations the cortex around this portion seems to be entirely free from continuation with the filamentous cells like a circumgenicular cortex of other species. But it would be a little

dangerous to give further details on this point, as the material worked over has been from a dried specimen. It might be stated, however, that at least a small portion at the base of the filamentous cells is not calcified and flexible as in the genicular portions of the other *Corallinæ*.

These peculiarities of structure suggest the convenience of omitting the above mentioned species from the general discussions of genicula. The following chapters will be applicable to the other members of the *Corallinæ*, except *Amp. aspergillum* unless it is specially mentioned.

### STRUCTURE OF GENICULAR CELLS AND COMPARISON WITH ARTICULAR CELLS.

The genicula of *Amp. dilatata*, *Amp. echigoensis*, *Amp. Bowerbankii*, *Amp. epherea*, etc.,—probably all members of the section *Eurytion*, Dene.—are built up with several zones of periclinal cells. The genicula of this category have special characters and should be treated further.

In *Amp. rigida* the genicula seemed to have been built up with two zones of periclinal cells. They are, however, always formed of a single zone, the cells being often intertwined at the equatorial points and looking like two zones. cf. *Cor. verae*. Jap. Pl. I. fig. 6.

The presence of the extragenicular portion is an important matter. Former investigators seem to have overlooked this. NELSON and DUNCAN<sup>1)</sup> remark that the long cells (of articulus) are often distinctly continuous with the filiform cellular processes of the articulations (genicula), especially with the deeply seated ones. They seem to have noticed nothing about the extragenicular portion. Among the multitudinous illustrations of “*Tabulæ Phycologicæ*”<sup>2)</sup> only two figures indicate this circumstance in any degree. And in

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1) l. c. p. 206

2) Vol. VIII Taf. 56. and 60.

the illustrations of “*Etude Phycologique*”<sup>1)</sup> and “*Sur les Corallines*”<sup>2)</sup> no precise point about it is given.

To begin with, we will treat of the unizonal geniculum; that is to say, a geniculum built up with a single zone of periclinal cells.

The genicular cells are long filamentous cells, varying in the proportion of their length and their diameter according to whether they take the middle or the peripheral position in the geniculum. The diameter of the cells is constant or nearly constant in a species. The part at both ends which I have called “extra-genicular portion” has mostly a different diameter from the genicular portion proper. The diminishing or the increasing of the diameter occurs abruptly at the critical points between the two portions.

In regard to the length of the filaments, we find that it varies according to the species; but it is always several times, often more than twenty times, as great as the breadth. We can not tell the proportional length by the mere external appearance of a geniculum. This is owing to the relative size of the circumgenicular cortex.

In the cross sections of the genicula we find the cells more or less polygonal from mutual compression. The cell rooms are comparatively narrow and mostly roundish polygonal.

Staining with colouring materials, we can easily perceive the lamellar structure of the cellwall in the genicular cells. The comparison of the properties of the wall with those of the articular cells is highly interesting. In the present paper it is not the aim to give the details of the microchemical properties of the cellwall, but some remarkable features we shall not fail to point out hereafter.

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1) BORNET et THURET: *Pl. L-II*.

2) DECAISNE: *Pl. 17*, fig. 5



When stained with BOEMER'S hæmatoxylin and fuchsin after the method I mentioned in my former papers,<sup>1)</sup> we find at least three lamellæ stained in different degrees. The innermost lamella is pretty thick, sharply distinguishable from the other parts of the wall (fig. 13). This part stains deepest in dark violet. It is the thickest of the lamellæ and is peculiar to the genicular portion proper. The genicula of the *Corallinæ* stain in a much deeper degree than the articular part. This circumstance depends upon the property of this lamella. The second lamella envelops the innermost lamella and varies in its thickness, as it seems, according to the age of the genicula. It stains in pale violet or grayish blue. At the external part of the latter lamella we have another thin lamella. This thin lamella practically answers the middle lamella of the higher plants and is clearest at the peripheral portion of the genicula; and in some species it is entirely invisible at the interior part of the genicula (fig. 14). In *Cor. yenoshimensis* the three lamellæ are very clearly defined (fig. 13). As the cells are more or less polygonal and compressed by each other, the outermost lamella is comparatively thick at the points where more than two cells meet together. In some species this lamella is to be detected only at these points (fig. 14). In the genicular cells of *Amp. stelligera* only the outermost lamella gives a deep violet colour, while the other portions remain a light bluish colour.

A peculiar modification of the wall was observed in the peripheral portion of a geniculum which had been attacked by a parasitic alga. The middle lamella stained exceedingly deep, while the second lamella was quite indifferent to the colouring material (fig. 15). At first the writer was induced to consider it the extra-genicular portion cut lengthwise. But the staining mode is just contrary to the ordinary case, and a further examination of the longitudinal section

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1) *Cor. vere* Japon. P. 3: *Cor. vere* of Port Renfrew P. 711.

showed that this modification was due to the parasitic *Diatom*. The exact determination of the parasite is beyond the present purpose.

When the section had been treated in anilin blue for 24 hours, we gained a beautiful preparation stained metachromatically. The outermost layer which fills up the intercellular space and apparently takes the place of the middle lamella stains in deep purple. The next layer stains in light blue. The innermost layer which stained in deep violet in hæmatoxylin is now separable into two parts. The innermost is very thin, but stains in deep purple; the outer layer in purple also but more faint. These two layers stained in the same degree when treated with hæmatoxylin.

Hence we might divide the cellwalls of the genicular cells into four parts, with the exception of those of *Amp. stelligera*.

I. *The middle lamella*: filling up the intercellular spaces and often hardly distinguishable at the axial portion of geniculum by virtue of the strong mutual compression of the cells: staining deep in hæmatoxylin and anilin blue.

This lamella corresponds in its position, especially when it is very thin, to the intercellular substance of DIPPEL.<sup>1)</sup>

II. *The primary cellwall*: staining in less degree with the colouring matters. With hæmatoxylin it stains in pale violet and with anilin blue in light blue.

III. *The secondary lamella*: staining in deep violet with hæmatoxylin, and in pale purple with anilin blue. It is this lamella which characterises the genicular cells when stained with the colouring materials. It stains much deeper than other parts in almost all colouring reagents.

IV. *The tertiary lamella*: staining in hæmatoxylin and anilin

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1) DIPPEL: Die Neuere Theorie über die feinere Structur der Pflanzenhülle.

blue very deep. When stained with the former it can not be distinguished from the second lamella: very thin: taking the innermost position of cellwall. Often this lamella can hardly be detected.

The extragenicular portion has several different characters in comparison with the genicular portion proper. The wall of the former part is not as thick as that of the latter, and there is always, after preparation, a longitudinal space left between each cell. When stained by an ordinary colouring reagent, this space remains unstained, apparently suggesting the intercellular space. When, however, the sections were treated in ruthenium red by the proper method, this space assumed an intense red colour. It is beyond doubt that the space is filled with a substance which has a peculiar character.

The cellwall of the extragenicular portion consists essentially of the continuation of the primary cellwall of the genicular portion proper. Its colouring reactions are always the same. And at the same time we do not doubt that this primary cellwall is that from which is constructed the whole framework of the articular cells. At the inner part of the wall we have a thin layer, which it is difficult to detect in some case, and which continues to the secondary lamella of the genicular cells. The thickness of the secondary lamella increases abruptly at the critical points between both the extragenicular and the genicular portions.

The extragenicular portions of the genicular cells, as has been formerly mentioned, contain deposits of calcium carbonate, while the genicular portions proper are destitute thereof. We often meet with preparations which have the genicular portions much shrunken and the extragenicular portions remaining in the original state. In those preparations we find the primary cellwalls of the genicular portions much fimbriated near the transitional points. This is probably due to the difference in the properties of the primary cellwall and the

secondary lamella : the walls of the genicular cells, the greater part of which is built up with the secondary lamella, contracting much more than the articular cells during the process of the preparation.

The middle lamella at the genicular portion proper stains intensely with ruthenium red, in the same degree as the apparent space just mentioned above. There is no doubt that both parts are continuous, although they are in some species entirely interrupted at the critical points. The space between the extragenicular portion of the cells is continuous to the intercellular spaces at the articular portion.

When a section of *Amp. tuberculosa* is stained in hæmatoxylin for a long time, say 24 hours in BOEMER'S, and treated with acetic acid thoroughly, we have a preparation stained in a contrary manner. The easily stained portions are easily washed away by the acid, and the articular cells which are hard to stain in the usual method now appear in a rather deep colour. The primary cellwall at the transitional point remains almost unstained and the distal ends of the extragenicular portion stain in the same degree with the articular cells. This fact shows something different in the properties of the primary cellwall in the transitional part and in the distal end of the extragenicular portion.

In this sort of preparation, the part of the primary cellwall in contact with the space mentioned stains intensely, cf. fig. 4. When treated with safranin the part now stained deep gains a yellowish colour.

It would not be useless to give some brief account of the middle lamella of the articular cells. The middle lamella of the extragenicular portion is practically continuous with that of the articular cells. When stained with ruthenium red, the part in connection with the genicular cells stains in the highest degree. The middle lamella of the articular

cells also stains clearly. Its thickness, however, is far less than that of the extragenicular portion. *Cheil. anceps*, *Amp. tuberculosa* and several species of *Corallina* have the periclinal cells running longitudinally but undulating; and their zonal arrangement is much disturbed (fig. 4). In these plants there are spacious rooms between the cells whenever the latter become parted. The middle lamella does not fill up these rooms and intercellular spaces in an exact sense are met with.

The cellwall of the periclinal cells at the medulla stains in some degree with ruthenium red, but those of the cortical cells in most cases remain unstained. In *Amp. tuberculosa* the genicular portion proper stained in only a very slight degree. But in most others the portion stains as deep as the cellwall of the medullary cells of the articulus. The cells at the circumgenicular cortex with its epidermal cells also have their cellwall stained in the deepest degree.

The genicula of *Amp. dilatata*, *Amp. ephedra*, *Amp. Bowerbankii*, *Amp. echigoensis*, etc., probably all of the *Eurytion*, are built up with several zones of periclinal cells. I would call them multizonal genicula to distinguish them from the unizonal ones. They are widely different, in construction and formation, from the unizonal genicula.

The number of zones which share the formation of a geniculum in this category, varies according to the species and the individual. In *Amp. dilatata* the writer counted 15 zones (fig. 5) and in *Amp. ephedra* only 4 (fig. 6). In every case there is more than one zone. SOLMS-LAUBACH<sup>1)</sup> remarked that the genicula of *Corallina* are built up with single layer of periclinal cells but those of *Amphiroa* always two layers. The present writer met with a number of instances which disprove the latter part of his remark.

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1). *Corallina* p. 29.

These zones as a whole does not form the geniculum ; but some of the zones, at both ends, share only partly. The zones of the periclinal cells, as has been already remarked, are concentric arcs, convex toward the apex of the frond. The boundaries of the geniculum, on the contrary, are very often convex toward the base. The consequence is that some of the zones partly share the geniculum (figg. 5-6). This fact has been formerly noticed by the writer in his paper "*Cor. veræ Japon.*" (Pl. 1. fig. 21).

The genicula of *Amp. stelligera* and its allies are also constructed with a number of zones. Differing from the other multizonal genicula, the critical part between the articular and the genicular portion is much like the case of the unizonal genicula ; that is the ultimate ends of the distal genicular cells are differentiated into peculiar parts, corresponding, though not sharply, to the extragenicular portions of the unizonal genicula.

The staining material act upon the genicular cells in a similar manner as in the case of the unizonal geniculum. Hence we may easily point out the genicular portions with the naked eye when we stain the frond *in toto* after decalcification. In the apical portion of the fronds where the genicula have not yet been completely built up, we can tell exactly the future genicula by this method. cf. *Cor. veræ Japon.* Explanation of Pl. 1. fig. 21.

The cellwall of the genicular portion proper consists of the four lamellæ as in the case of unizonal genicular cells. The tertiary lamella, however, is sometimes very hard to detect. Almost all the members which belong to this category have the bordered pits in the lateral sides of the cells, besides the connecting pits at the distal ends of the periclinal cells. These bordered pits are not perforations between the cells but are septed by thin membranes of the middle lamella. They are, as a rule, in rows parallel to the zones and are

situated at the distance of about one-third of the length of the cells from the upper ends of the cells (fig. 11). In *Amp. dilatata* the tertiary lamella is remarkable in the part below the pits. This circumstance causes the upper one-third of the cells to stain in a less degree. Hence the longitudinal section of the geniculum, after staining, shows alternate parallel curves of faint and deep coloured zones (fig. 5).

In some cases we find transverse dissepiments in the periclinal cells (fig. 6). This character has never been hitherto found in the unizonal genicular cells, as far as the writer could observe. We shall give some account of these dissepiments in a later chapter.

The difference of the property of the cellwall at the genicular and the extragenicular portions is also remarkable in this case. As a rule, the cellwall at the genicular part is thinner than the extragenicular portion. The difference of the thickness occurs abruptly at the point of transition from one to the other. The decrease of thickness is essentially due to the primary cellwall. The middle lamella stains deep with hæmatoxylin at the genicular part; the primary cellwall in a less degree and the secondary (sometimes together with the tertiary) lamella stains in intense violet. In the extragenicular portion the middle lamella stains much weaker, and the secondary lamella is almost wanting here (fig. 11).

I have called it extragenicular portion here. But the area mentioned under the name is somewhat different from the case of the unizonal geniculum. As might be well understood from the structure of the genicula under treatment, there is no special portion which corresponds to the extragenicular portion of the unizonal genicula. The parts in contact with the articular portion, from the morphological point of view, have no special differentiation. A part, however, of each cell just related to the genicular portion is destitute of starch grains. The nourishment is probably consumed during the formation

of the geniculum. This phenomenon, of course, undergoes much fluctuation according to the condition of the genicula.

In *Amp. aspergillum* we find the lower half of the filamentous cells stained much deeper with hæmatoxylin than the surrounding regions. The upper zones, that is, the layer of the elliptical cells at the upper end of an articulus, stain in the same degree as the upper half of the filamentous cells. The elliptical cells have cellular connections at the distal ends and at the periclinal sides; and the transverse communication between the filamentous cells is confined to the uppermost part of the periclinal side.

### Formation and development of the Geniculum.

The formation of the geniculum takes place at an early period of the development of the frond. The first geniculum is already perceivable when the process of the frond has reached 1 mm. above the incrustation.<sup>1)</sup> As the frond grows higher, a geniculum is formed just below the apex of the frond.

The apical growth of the *Corallinar* depends upon the division of the cell layer which covers the apex of the frond.<sup>2)</sup>

As far as the writer could observe, the genicular cells are not directly formed from the layer of the growth. The search for the youngest geniculum directly under that layer ended without success; but it was found always at a distance from the apical point. Several zones of the periclinal cells are generally found lying between the new geniculum and the apex. In the case of multizonal genicula this is especially the case, and in hair-like *Jania* the genicula are close to the apex.

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1). HEYDRICH: l. c. p. 79. Taf. 11. fig. 23.

YENDO: Cor. vere Japon. Pl. 11. fig. 5.

2). SOLMS: l. c. p. 29.

KNY: Ueber echte u. falschedichotomie im Pflanzenreich.



By careful study of the shape, position and the length of the cells of the genicula, the writer arrived at the conclusion that the genicula are transformed from the zone or zones of the matured periclinal cell.

In normal cases the cells sharing the formation of a geniculum are limited to the medullary cells. An exception is the genicula of *Amp. stelligera* and its allied species. In these species the long filamentous genicula are formed of several zones of the medullary cells, generally much disturbed in the cellular arrangement. These genicula are coated with cortical layers from the beginning of their formation. In these species the cortical layers around the zonal cells play an important part in giving rise to the primary genicula of the whorly ramules.

Another example of a geniculum with cortical layers is found in certain species of the *Eurytion*. In this, the greater part of the overlying cortical layer is dropped off in the process of the genicular formation, which is described below; but those cortical cells closely adhering to the genicular cells remain as such. These cortical cells have similar characters with the genicular cells in every way and last as long as the genicula exist.

The primary geniculum of a ramule in *Amp. aspergillum*, *Amp. calonioides*, etc. is apparently transformed out of the cortical layers. These are, as a matter of fact, built up by a similar process as that by which the primary geniculum of the main stem started from the incrustation. The primitive stage of the ramules is a mamillary process on the surface of an articulus. It is built up with a number of layers of globular or rectangular cells not distinguishable from other cortical cells. As the process elongates upwards by the intercalary growth of the cells of one or more layers, the geniculum is transformed from one of the elongated cell layers. The cortical layers, at least the

innermost one, remain in the original state. cf. pl. 1. fig. 3. *Cor. veræ Japon.*

The unizonal and the multizonal genicula differ genetically. In the following paragraphs we shall try to give some details of the development of both.

One of the youngest geniculum formed from the single zone of the periclinal cell is illustrated by the writer in "*Cor. veræ Japon.* Pl. 1. fig. 2. The figure shows a longitudinal section of a branched frond of *Amp. calonioides*. The geniculum of the branch is much younger than that of the axial stem. The genicular cells are hardly longer than the ordinary vegetative cells, with the circumgenicular cortex still remaining as such. The differentiation of the cellwall has already taken place in the genicular cells, staining the genicular portion proper in deep violet by BOEMER's hæmatoxylin. The geniculum is already free from the deposit of calcium, while the extragenicular portion is calcified as in the remaining part.

As a general rule, the sum of the extragenicular portions at both ends of the genicular cells is nearly equal to the average length of the periclinal cells of the artichus. In some species (*Cheil. anceps* and *Jania* species) the zonal arrangement of the periclinal cells is much disturbed. As a consequence, the extragenicular portions of the cells are very variable in their length. Those cells which have a comparatively short extragenicular portion at one end have in almost all cases a much longer portion at the other :—the sum of both portions being nearly equal in each cell.

This circumstance teaches us that a certain zone of the periclinal cells is divided into two parts along a plane perpendicular to the long axis of the cells. At the division plane the intercalary growth of the cells takes place, stretching the zone lengthwise. The cells elongate, without deposition of the calcareous substance, and with a new

addition of the secondary lamella. The middle lamella follows the growth, though it is much thinner than in the articular cells.

The growth of the cells seems to be of such great rapidity that the cortical cells around the geniculum can no longer bear the strain. The result is the cracking of the cortex.

Regeneration seems to take place at the overhanging margin of the circumgenicular cortex after the splitting has occurred. On the freed ends of the cortex we actually observe the remnants of the decayed cells which have broken during the formation of the fissure; and generally we find the cells in the circumgenicular cortex dividing in the anticlinal and periclinal direction (figg. 4, 6 and 10). This circumstance, no doubt, effects the "linear" genicula, exposing a comparatively smaller portion outside, the larger part of the length being hidden under the circumgenicular cortex.

The best developed example of the circumgenicular cortex is found in *Amp. stelligera*. In this species we find a highly thickened portion at each distal end of an artichulus. This thickening is due to the unusual increase in the number of the cells of the circumgenicular cortex. (fig. 8).

While the geniculum is yet very young or the development is not comparatively rapid, the cortical layers remain around the geniculum (fig. 5).<sup>1)</sup> These layers in most of the species are destined to drop off sooner or later. HARVEY<sup>2)</sup> describes a plant with calcareous granules upon the genicula. His plant had probably the circumgenicular cortex split into several pieces, remaining attached upon the surface of the genicula. Very often we find similar cases in several other species. Fig. 9, shows one case in *Cheil. frondescens*,

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1). See also Pl. I. fig. 3. *Cor. verae* Japon.

2). *Nereis Australis*; *Amp. Bowerbankii*, Harv. p. 97. t. XXXVII.

having a few cortical cells, of course calcified, yet remaining undetached.

In the unizonal genicula the cells undergo further development in only the slightest degree. The cells of the basal genicula of *Amp. aberrans*, for instance, have their length nearly equal to the upper ones and the thickness of their walls seems to have received no addition. SOLMS-LAUBACH<sup>1)</sup> observed the formation of transverse septa in the genicular cells of *Corallina*. These transverse septa were quite common in the genicular cells of the *Eurytion*; but, as far as the present writer could examine, there was no septum formation in the cells of unizonal genicula, to which category all of *Corallina* belong.

The formation of the multizonal genicula is fundamentally different from that of the unizonal. The first step is the decalcification of a certain part of the frond, bounding several zones of the periclinal cells. This process seems to be carried on in a comparatively short time. The boundary of the decalcified area is very sharp, and can be easily traced by a staining reaction after the frond has been artificially decalcified. The area seems not to extend further than the limit formed at the first step of the formation.

While decalcification is taking place, the cortex around it remains unaltered for some period. But afterwards a part of the cortex, mostly on the flat surface of the frond, comes off in shape more or less corresponding to the decalcified area. The result is the "fenestraform" geniculum.

As the geniculum develops further, the cortex around it continues to break off, until a complete "bandform" geniculum is visible to the naked eye.

As soon as the fenestraform has appeared, the genicular cells begin to undergo further modifications. It is the formation of the

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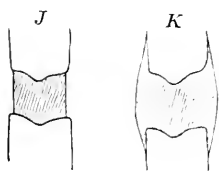
1). *Corallina*: p. 29.

transverse septa in the periclinal cells. These septa begin to appear first in the cells at the peripheral region (fig. 6).

In the beginning each genicular cell has two or three septa at nearly equal distances. As the process is carried on further, more septa are continuously formed between the old ones. At last the long fibrous cells are divided into a number of collenchymatous cells, with a much thickened membrane and scanty room. The zonal arrangement of the cells is much disturbed.

The peripheral cells which are now globular from the septation begin to form a secondary cortex. The cells continue to divide tangentially and the thickening of the wall increases further. The consequence is a thick layer of cortex, overlapping the distal ends of the articuli at both sides. The length of the geniculum at the axial portion does not very much exceed that of a young geniculum. We always find the large bandform genicula at the basal portions of the fronds in those species such as *Amp. dilatata*, *Amp. ephedrea*, *Amp. Bowerbankii*, etc. The width of the genicula is often larger than the length of the neighbouring articuli. This modification is due to the peripheral part of the genicula extending to cover the distal ends of the articuli. The accompanying figures J and K show the longitudinal sections of the fronds of *Amp. dilatata* through the genicula. Fig. J is a completed geniculum but without the secondary growth of the

peripheral cells; fig. K, is a rather old geniculum with the peripheral part of the genicula overlapping the articuli at both ends.



In these old genicula, the medially and the cortical portions are more or less distinguishable.

The former has the cells some what elongated and an obscure zonal arrangement of the cells is to be seen. The latter has cells with narrow rooms, thickened wall, and arranged in radial rows. The

thickening of the wall is accompanied by the formation of canals therein. The canals radiate from the center of the cells, some continuous to the canals of the neighbouring cells and some ending at the middle lamella. cf. *Cor. verae* Japon. Pl. 1. fig. 20, which illustrate the cross and the longitudinal sections of the medullary portion of an old geniculum.

The bordered pits are also modified by the thickening of the wall. At an early stage, only the canals which are modification of the pits are to be seen. But in the further advanced stage, a new formation of canals takes place by the thickening of the walls; so that we can not distinguish the canals of genetically separate origin.

These remarks do not apply to the genicula of *Amp. stelligera*, although they are built up with a number of zones. The cortical cells in these genicula remain persistent from the beginning and the zonal cells grow rapidly and increase in their number by transverse division. The cortical cells also accompany the growth and the multiplying of the cells. It is not certain how the primitive genicular are transformed from the calcified articulari. The presence of the extragenicular portions suggests the similarity of the mode of the genicular formation with that of the unizonal genicula. But already in a pretty young genicula, several zones of the periclinal cells have been clearly observed (fig. 8). I was not able to trace the origin of the genicula in the species, as the apical portions of the dried material are always due to the destruction of the cellular arrangement while imbedding in the paraffin. This must be kept for future study, until we have preserved material from fresh plants.

One thing which we must not omit mentioning here is that the primary genicula of the ramuli of *Amp. stelligera* are not directly connected with the articular cells but with the cells of the axial geniculum. Some of the zonal cells of the axial geniculum travel

obliquely upward and outward and protrude into the medulla of the primary genicula in the mode of emergence through cortical layers (fig. 8).

## The Difference in the Properties of the Cell-walls of Articular and Genicular Cells.

It was not the aim of the present paper to give a discussion in detail concerning the chemical properties of the genicular cells. In the course of study, however, some points which might interest the reader in some measure have been noticed about the differences in the properties of the cellwall of the articular and the genicular cells.

The calcareous matter is in the cellwalls of the articular cells. This has already been remarkable by former observers.<sup>1)</sup> The middle lamella seems especially rich in such matter. Although positive proof is lacking, this view is held from a microchemical examination of the cellwall, as will be described below. The mineral is in the form of fine ingredients mixed with other substances.

The cellwall of the genicular portion proper and the epidermal cells are entirely free from calcareous matter. The reproductive cells are, of course, similiary free.

The extragenicular portions of the genicular cells, and the articular cells, except the epidermis, have a calcified cellwall.

Briefly speaking, the cellwalls of the cells of the *Corallinæ* consist essentially of a compound of cellulose, gelose and lime. The proportion of the components varies according to the parts of the fronds. The energetic cells, such as epidermal cells of the grow-

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1). NELSON and DUNCAN. I. c. p. 199. and p. 205.

ing portions, the periphery, or the circumgenicular cortex, have a larger percentage of the pectin compound than of the cellulose. In this respect the growing points of the land plants furnish us an illustrious parallel. The middle lamella, especially at the extragenicular portion, and the connecting plates between the cells, are richer in the pectin compound. In phanerogamic cells we have calcium pectate in the middle lamella. In the present study the writer was not able to determine whether the middle lamella contained the mineral in the form of calcium pectate or calcium carbonate. Any how, the middle lamellae of the articular cells, as in the case of the phanerogamic cells, are very rich in pectin compound.

The cellwall of the genicular portion proper has several diverse characters. By iodine it gains a deep bright yellow colour, almost brownish. So far as the ordinary cellulose reagents are concerned, the cellwall of this portion gives no reaction of cellulose. It is not a chitinous substance. Probably the cellulose reaction might have been retarded by some compound other than the pectin. The middle lamella of this portion gives also a distinct reaction of a pectin compound. This leaves us in doubt whether a trace of calcium compound occurs there or not, although we can by no means detect it.

The pectin compound in the cellwall is in the form of gelose as in the other algal members.

The cellulose reaction is not discernible before the gelose has been dissolved. But the gelose reaction is clearly visible without any treatment beforehand.

When the preparations<sup>1)</sup> are treated with 50% hydrochloric acid for 12-24 hours, both the cellulose and the gelose reactions begin to appear. In these ruthenium red stains the primary cellwall of all

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1). The study has been made upon preparations cut by microtome in the thickness of 3-4 $\mu$ . The object is imbedded, after decalcifying in PERENY's fluid, in 52° paraffin.



parts in a greater or less degree; but the reaction is most vivid in the epidermal layer and in the cellwall of the subepidermal cells. The genicular portion proper retains a bright red colour. Treated with chloriodide of zinc, the epidermal layer assumes a deep yellow colour and the subepidermal cells have their cellwall stained in faint violet. The primary cellwall in every part becomes stained in violet. The middle lamella remains unchanged. The starch grains in the medullary cells assume a chestnut brown colour, while the cellcontents in the subepidermal cells change only to yellow. The genicular portion proper stains in deep brownish yellow. The gelose reaction by ruthenium red is seen without treating with hydrochloric acid, but chloriodide of zinc can never act upon the cellwall of the articular cells before the treatment with the acid.

Before treatment with hydrochloric acid the cellwall gives no reaction either by strong caustic potash or by potassium iodide iodine and sulphuric acid.

After boiling the sections in 2% hydrochloric acid for a few minutes, washing thoroughly in water, and again boiling in 2% caustic potash, a few drops of chloriodide of zinc were poured in under the coverglass; epidermal layer stained in bright yellow and the cellwall of the subepidermal cells in a slight degree. The cellwall of the articular cells gains a yellow tint, but the middle lamella of these, which was much swollen during the process, stains in pale violet. The connecting plates between the cells become exceedingly clear: the central portion of them staining in deep brown and the border in bright yellow. A preparation boiled in like manner was treated in ruthenium red. The middle lamella, if not swollen too much, is stained in some degree, the swollen portion remaining unstained: the connecting plates assume a red colour and their central portions in a greater degree.

When treated in 50% hydrochloric acid for 48 hours, the gelose reaction becomes fainter. The epidermal layer stains no more with ruthenium red; the middle lamella at the articular portion in some measure; and the cellwall of the genicular portion pretty strongly. On the other hand the genicular cells are stained deep brown by chloriodide of zinc and the middle lamellæ of the articular cells and of the extragenicular portions assume the deepest brown colour. The cellwalls of the articular portions, inclusive of the extragenicular portion, assume a deep violet. The epidermal layer gives no reaction with chloriodide of zinc.

Keeping 5 days in 50% hydrochloric acid, I observed the reactions. None of the parts was stained by ruthenium red. By chloriodide of zinc the middle lamella stained in deep violet, especially at the extragenicular portion. The cellwall of the genicular portion proper stains in deep brown, but nothing of a violet tone. The preparation thus kept was treated with copper ammonium oxide for 48 hours. The result was the entire dissolution of the sections except some of the genicular portion proper. This remnant when treated with chloriodide of zinc gives a brownish colour. Some of the preparations had been kept in copper ammonium oxide for 20 hours previous to the treatment with hydrochloric acid, the cellwalls of the articular portion were almost all dissolved, leaving the epidermal cells behind. The middle lamella of the genicular cells remained unchanged, but the cellwalls were almost gone.

I would point out some minor details which were met with during the treatments above mentioned, by the staining reactions of anilin blue, hæmatoxylin, safranin, etc.

The intercellular space in the articular cells is some times filled by the middle lamella, the so called intercellular substance of DIPPEL;<sup>1)</sup>

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1). Die Neuere Theorie über d. feinere Struct. d. Pflanzenhülle.

sometimes it is free from any packing. These differences depend upon the species. In some species which have no true spaces between the cells, the middle lamella has a considerable thickness ; in those which have the rooms, the middle lamella is found adherent to the primary cellwall around the room. In either case the middle lamella runs into the genicular portion proper, often much compressed at the critical point and hard to detect. The middle lamella at the genicular portion proper is almost always much thinner than in the articular portion. The middle lamella is rich in pectin compound and stains very well with hæmatoxylin, safranin, anilin blue and ruthenium red.

The primary cellwall supplies the greater part of the framework. When the pectin compound had been dissolved by proper treatment, the cellulose reaction was seen in this part. An exception is the cell-wall of the subepidermal layers : it makes no response to the cellulose reagents, but gives us a vivid gelose reaction.

The primary cellwall of the articular portion is continued to that of the genicular portion proper. It becomes much thinner when it enters the latter portion and seems to assume a chemical character different from the articular portion. This conclusion is reached from its giving no cellulose reaction even after long treatment with the gelose solvent. It is stained a pale blue by anilin blue and faint violet by hæmatoxylin. Ruthenium red stains it light red.

The secondary lamella lines the inside of all the cells and has a character similar to the middle lamella against the chemical and the staining reagents. It runs into the genicular portion proper and a secondary thickening takes place to form the tertiary lamella. These two layers are essentially equal in their character and hardly distinguishable in ordinary reagents. But when stained with anilin blue, the inner layer gains the deepest purple colour and is easily

distinguishable from the other. The tertiary lamella is characteristic of the genicular portion proper.

The lamellar arrangement of the cellwall in *Amp. dilatata* and its allied species comes under a somewhat different category. The tertiary lamella is only visible in the lower two thirds of the cells of the genicular portion ; in other words the parts below the row of the pits (figg. 11-12). It is hard in these species to recognize the layer which corresponds to the secondary lamella of the other members. On the other hand, a characteristic lamella is found at the meeting point of the cells, which are always eight in number. The lamella develops at the corner of the cell toward the center of the intercellular space to fill it up. This lamella has some space between it and the mother cellwall where some substance easily stained with hamatoxylin is always found (fig. 12).

The majority of the *Corallineæ* have connecting plates at the distal ends of the cells both at the medulla and at the cortex. These plates show the characteristic reaction of the pectin compound, while the cellulose reaction is hard to detect. The connecting plates at the articular ends of the extragenicular cells are especially rich in the pectin compound.

Those species which have conspicuous canals or rather perforations between the cells have their plates in the form of thin septa. But when the canals are narrow passages, the colouring materials fill up the passages and prevent us from determining precise form of the septa.

In many species we often find large openings to allow the communication between the cells. cf. *Cor. vera* Japon. Pl. II. figg. 21 and 23. These large openings seem to lack any kind of connecting plates. SCHMITZ<sup>1)</sup> observed the protoplasm of the neighbouring cells

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1). Untersuch. ueber d. Zellkern d. Thall. p. 122.

communicating with one another through the pores in *Jania rubens*. WILLE<sup>1)</sup> also mentions this character and seems to believe that probably all species of *Amphiroa* and *Corallina* have the same sort of pores. As will be understood from the present study, the pores in the cell-walls are limited to a certain group of the *Corallinæ*. Some of *Amphiroa* have the pits and most of the *Eurytion* have the bordered pits. This will be described more in detail.

*Amp. dilatata*, *Amp. Bowerbankii*, etc., are those which have the bordered pits. These pits are found at the distal ends of the periclinal cells in like manner as the connecting plates in the other species, and also at the periclinal sides of the cells. They are exactly similar in the structure to those found in the *Conifers* (fig. 12). The large openings just mentioned above are not met in these species.

The bordered pits in the periclinal sides are almost always at points nearly one third of the length of the cells from the upper ends, as has been formerly remarked. Hence the pits, in a meridional section of a frond, are seen disposed in rows parallel to the zones of the cell connection. About the fate of the pits a brief account has already been given (p. 32).

There is an interesting parallelism in the pits of the land plants and the *Corallinæ*. In the land plants the pits are normally found in such groups as *Conifera*, *Drimys*, *Trochodendron*, etc., which are provided with poor vessels or none at all.<sup>2)</sup> It has not been hitherto described, as far as the present writer's knowledge extends, in the lower cryptogamic cells. The principal part of the translocation of the nourishment is played through the thin membrane of the pits. *Algae* as a whole have no kind of the vessels and all communication must be furnished by the openings between the cells. And these

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1). Bidrag till Alg. Phys. nat. p. 40.

2). STRASBURGER: Ueber d. Bau u. d. Verrichtungen d. Leitungsbahnen. p. 161.

openings septated or non-septated, are always met in the cells of the *Dictyotale*, the *Florideae* and many of the *Phaeophyceae* and some of the *Chlorophyceae*.

I have already mentioned in connection with *Amp. dilatata* (p. 25) that the cell contents in the surrounding cells of the geniculum are consumed. This may possibly always be the case in the other members. The cell contents are in greater part Florideae starch. There is little doubt that the starch is transformed into a soluble hydrocarbon and carried on through the thin membrane of the bordered pits to be consumed during the formation of the geniculum.

### The Value of the Geniculum as a Systematic Character.

The presence of the genicula has been counted as the crucial point in distinguishing the *Corallineae* from the *Melobesia*. But little heed has been given to the systematic value of the geniculum in the study of the *Corallineae*. The external shape of the articuli, which is undoubtedly highly variable, has been the important specific character; and the position of the propagating organs played a weighty rôle in the generic determination. The mere external appearance of the genicula has sometimes been mentioned by writers in describing the species.

The internal structure of the genicula, however, has some coincidence with the external morphological characters. SOLMS remarked the difference between the genicula of *Corallina* and *Amphiroa* as noted before (p. 23). But we found many examples which disprove his observation: some of the species reckoned under the genus *Amphiroa* have unizonal genicula, and some multizonal, as has been

related in the preceding chapters. KÜTZING<sup>1)</sup> insisted upon the view that the difference of the internal structure might serve to determine the genera of the *Corallinæ*. This is not absolutely true. But some of the members, probably almost all, of a section established by DECAISNE<sup>2)</sup> have common characters in respect of the internal structure. For instance, as would be already understood, most of the *Eurytion* have the bordered pits in the cellwall, and multizonal genicula which undergo further development. Most of *Jania* have the zonal arrangement of the periclinal cells irregular, and the unizonal genicula. And *Cheilosporum*, especially the *Eucheilosporum*, has a similar character to *Jania* in this respect. But we can not agree with the opinion that *Amp. stelligera* which has the peculiarities in the structure, as well as in the function, of genicula should be classified under the genus *Amphiloa*. So also *Amp. aspergillum*.

It should be admitted that the morphological characters, both of inner and outer, of genicula may play some important part in systematic survey. It may not be a generic character ; but at least a group may be more sharply defined by the peculiarity, of any, of genicula, rather than by mere external forms of articuli. The position of the genicula in a frond has sometimes a unique character and may well play a part of specific importance.

These views, together with those of the former writers, are reserved for future discussion.

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1). Ueber die Polyp. Calcif.

2). Classif. des Alg. et des Polyp.

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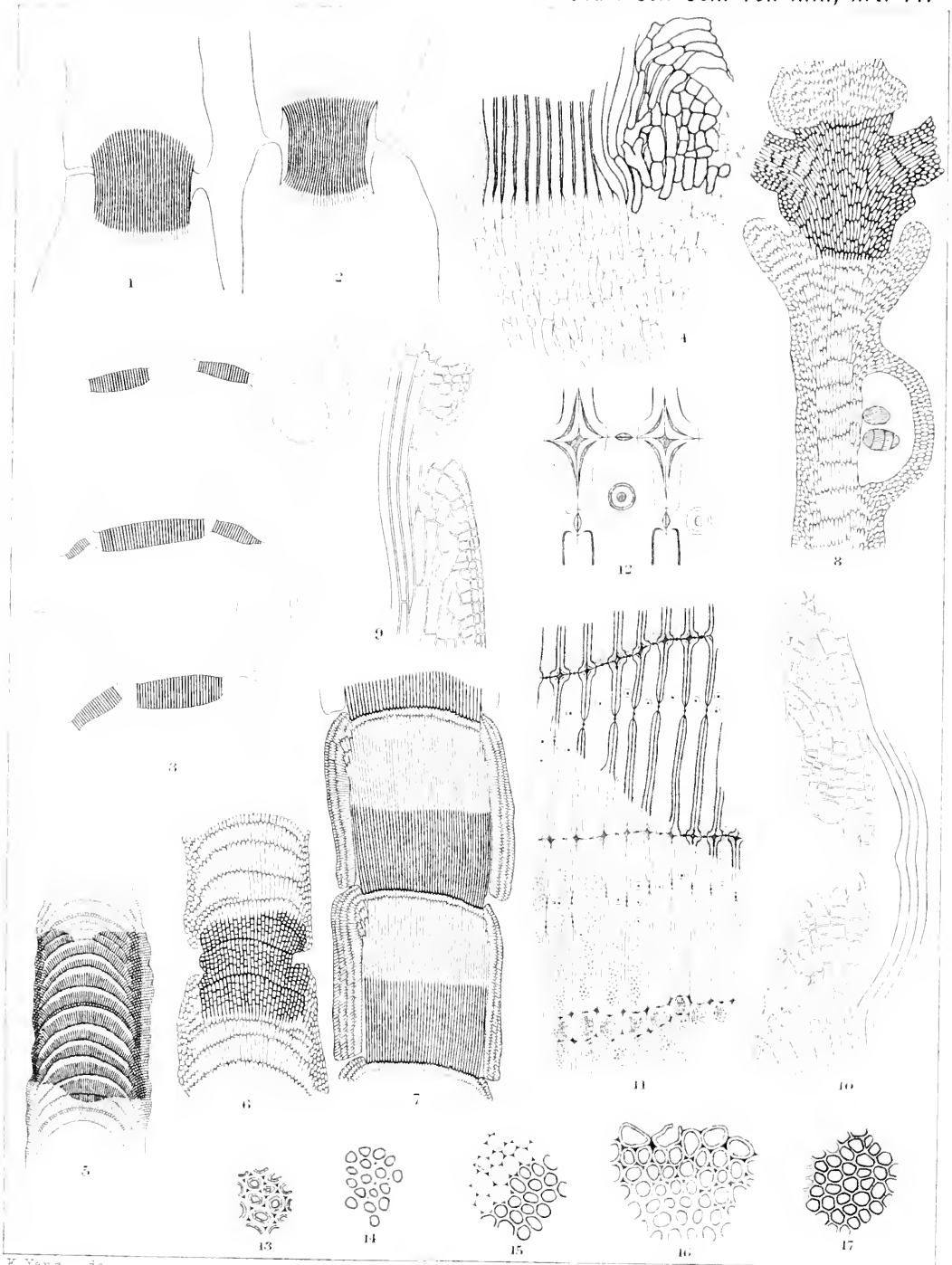
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PLATE.

## EXPLANATION OF PLATE.

All figures are Camera drawings, with the exception of fig. 12.

1. Longitudinal section of a frond through a geniculum ; *Corallina chilensis*. The extragenicular portions of the genicular cells are shown by the fine lines.  $\times 60$ .
2. do. *Cheilosporum frondescens*.  $\times 60$ .
3. Longitudinal section of a frond of *Amphiroa aberrans*. Observe that the genicula of the axial articulus and of pinnae originated from different zones.  $\times 40$ .
4. Longitudinal section of a frond through geniculum ; *Cheilosporum anceps*. The shaded portions gain a deeper stain from the colouring reagents.  $\times 285$ .
5. A meridional section of a frond through the young geniculum ; *Amphiroa dilatata*.  $\times 40$ .
6. do. *Amphiroa ephæra*.  $\times 40$ .
7. Longitudinal section of a frond of *Amphiroa aspergillum*.  $\times 40$ .
8. do. *Amphiroa stelligera*.  $\times 60$ .
9. Longitudinal section of the circumgenicular cortex of *Corallina chilensis*.  $\times 165$ .
10. do. *Cheilosporum frondescens*.  $\times 165$ .
11. A portion of fig. 5.  $\times 650$ .
12. The meeting points of the genicular cells of above : highly magnified.
13. Cross section of the genicular cells of *Corallina genoskimensis*.  $\times 285$ .
14. do. of *Amphiroa aberrans*.  $\times 285$ .
15. External portion of a geniculum attacked by parasitic *Diatom* : cut lengthwise : *Amphiroa aberrans*.  $\times 285$ .
16. External portion of a geniculum of *Corallina chilensis* : cut lengthwise.  $\times 285$ .
17. Cross section of a geniculum of *Amphiroa aberrans* : about the middle portion.  $\times 285$ .





**Peroxylaminesulphonates and Hydroxylamine-  
trisulphonates (Sulphazilates  
and Metasulphazilates, Fremy).**

By

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Imperial University, Tokyo.*

Perhaps the most interesting of the sulphazotised salts discovered by Fremy (*Ann. Chim. Phys.*, 1845, iii, **15**, 408) are the two which result from the oxidation of one or other of the potassium hydroximino-sulphates (hydroxylaminedisulphonates) in aqueous solution by either silver oxide or lead peroxide or some other reagent. One of these products is the very unstable salt which he named *sulphazilate*. It is remarkable for crystallising from its aqueous solution, which is of an intense bluish-violet colour, in brilliant golden-yellow needles, very slightly soluble in ice cold water, but easily dissolving in hot water. It can seldom be long preserved and gives a disagreeable odour to the skin, like that caused by manganates and ferrates. According to Fremy, it is easily fusible, but that is a mistake; it is the products of its decomposition which melt. The other salt, his *metasulphazilate*, is also sparingly soluble in cold water, but is colourless and has considerable stability. It crystallises in rhombic prisms which are so well defined that Fremy describes the compound as being the most beautiful of all the sulphazotised salts. These crystals appear to be isomorphous

with those of 5/6-normal potassium hydroximosulphate, and the two salts can hardly be separated by crystallisation. Its solution is quite neutral and gives a precipitate with basic lead acetate only. Fremy expressed the composition of the sulphazilate by the formula,  $\text{HO} \cdot \text{NS}_2\text{K}_2$  (here written with the atomic proportions now in use), which is only incorrect in including hydrogen (Claus). He gave the composition of the metasulphazilate correctly as  $\text{H}_6\text{O}_{23}\text{N}_2\text{S}_6\text{K}_6$ .

Claus (*Annalen*, 1871, **158**, 205) who gave details for the preparation of the coloured salt by lead peroxide, proved that in its production from 5/6-normal potassium hydroximosulphate it is not necessarily accompanied by sulphate; he also demonstrated with tolerable certainty that it is the sole product of the oxidation; and found that it passed spontaneously into the colourless salt, together with a fixed quantity of sulphate and a gas which is apparently nitrous oxide (compare page 16 of this paper). He recognised the sulphonate constitution of both salts and gave to the coloured salt the name and formula, 'oxysulphazotate,'  $(\text{SO}_3\text{K})_3\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{O} \end{array} \text{N}(\text{SO}_3\text{K})$ , and to the white salt the name and formula, 'trisulphoxyazoate,'  $\text{O}:\text{N}(\text{SO}_3\text{K})_3$ ,  $\text{H}_2\text{O}$ , that is, with the nitrogen quinquevalent in both formulæ. It will be seen that, even empirically these formulæ differ a little from Fremy's. Claus also sought for, and, as he believed, obtained the primordial sulphazotised salt, which he formulated at first as  $\text{SO}_2\text{NO}_2\text{K}$  (*op. cit.*, 213), and afterwards as  $\text{O}:\text{N}(\text{SO}_3\text{K})$  (*Ber.*, 1871, **4**, 508). This would be the analogue of the 'trisulphoxyazoate,' only with the nitrogen trivalent; but the existence of this salt has since been disproved (this Journ., 1900, **13**, 219).

Raschig (*Annalen*, 1887, **241**, 223) having found that the white salt, in a boiling and feebly acid solution, may yield sulphate to the extent of two-thirds of its sulphur, along with, apparently, hydroxyaminosulphuric (hydroxylaminemonosulphonic) acid, has recognised that



it behaves as a derivative of hydroxylamine. But, because it does not decompose when in strongly alkaline solution, he will not allow that it is that base trisulphonated. He modifies Claus's two formulae, writing that for the coloured salt as  $(\text{SO}_3\text{K})_2\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{N}(\text{SO}_3\text{K})_2$ , and that for the white salt as  $(\text{SO}_3\text{K})_3\text{N} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{N}(\text{SO}_3\text{K})_3 \cdot 2\text{H}_2\text{O}$ .

Hantzsch and Semple have found (*Ber.*, 1895, **28**, 2744), that, when crystals of 2/3-normal potassium hydroximiniosulphate form in a bluish-violet solution of potassium sulphazilate, they may contain 1–4 percent. of this salt, apparently in solid solution, and consequently show bluish-violet colour. These chemists have therefore advanced the view that Fremy's coloured salt, which they have re-named 'nitroxydisulphonate,' is sulphonated nitric peroxide, the orange-yellow crystals of which have double the molecular magnitude of its dissolved bluish-violet form, in analogy with the two forms of nitric peroxide itself. The formula for the bluish-violet modification is given in a foot-note as  $\text{O}:\text{N}:(\text{SO}_3\text{K})_2$ , in which, therefore, the nitrogen is represented as being trivalent and the oxygen as univalent. A structural formula for the yellow modification is not given, but Raschig's is rejected, as having two quinquevalent nitrogen atoms in union with each other, a mode of combination which is without parallel. Raschig's formula for the white salt is also rejected, but as the simpler one proposed by Claus is adopted in its place, the quinquevalency of the nitrogen is maintained. On the authority of Schatzman, and as a result of their own experiments in the case of hydriodic acid, these chemists state that, in acting as an oxidising agent, the coloured salt reverts to hydroximiniosulphate.

In 1896, Sabatier (*Compt. rend.*, **122**, 1417, 1479, and 1537; **123**, 255) published the results of an investigation of the violet solutions produced by reducing agents acting on a sulphuric acid solution of nitrososulphuric acid, and suggested that the colour is due to the

formation of the acid of Fremy's potassium sulphazilate. His suggestion is discussed on page 22 of this paper.

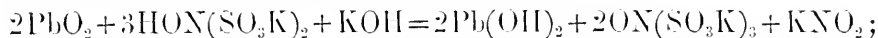
In the detailed examination of Fremy's sulphazotised salts made by Dr. Divers and the author, the results of which have been described from time to time in this Journal, the sulphazilate and metasulphazilate were purposely reserved for separate treatment, because they are distinguished from the other salts in being products of oxidation. In the present paper the author endeavours to prove (1) that the sulphazilate is an *oxime-peroxide* (Scholl) or a *peroxime*,  $(\text{SO}_3\text{K})_2\text{NO}\cdot\text{ON}(\text{SO}_3\text{K})_2$ , the first and only inorganic peroxime yet known; (2) that the metasulphazilate is a *triacylated hydroxylamine*,  $(\text{SO}_3\text{K})_2\text{NO}(\text{SO}_3\text{K})$ , the only compound of this type having an established normal constitution (all others, such as tribenzhydroxylamine, being apparently of more complex constitution); and (3) that, consequently the nitrogen, in both these sulphazotised salts is only trivalent, instead of being quinquevalent.

From among the several constitutional names which suggest themselves for Fremy's provisional 'sulphazilate' and 'metasulphazilate,' that of *peroxylaminesulphonate* for the former, and of *hydroxylaminetrisulphonate* for the latter, have been adopted as preferable. In consequence, it has been found advantageous in this connection to call the parent salt *hydroxylaminedisulphonate* instead of the alternative *hydroximinisulphate*, the name usually employed by Divers and the author. It has also been found to be convenient to treat of the hydroxylaminetrisulphonates before the peroxylaminesulphonates, from which they are apparently always derived.

*Hydroxylaminetrisulphonates*  
(*Metasulphazilates*; *Trisulphoxyazotes*).

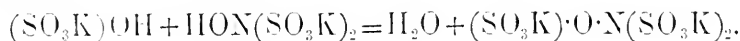
Potassium hydroxylaminetrisulphonate is most readily prepared

by Fremy's method, in which no intermediate separation is made of its parent salt, the peroxylaminesulphonate. Somewhat alkaline potassium hydroxylaminedisulphonate is gently boiled and shaken with silver oxide or lead peroxide, until the solution, which at first becomes intensely bluish-violet, just loses its colour. Then, by evaporation and cooling, the filtered solution can be made to yield nearly all its hydroxylaminetrisulphonate. Theoretically, all the hydroxylaminedisulphonate should be converted into hydroxylaminetrisulphonate and nitrite,



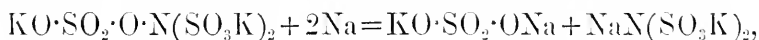
but sulphate and nitrous oxide are always produced, usually accompanied by very small quantities of nitrogen and aminemonosulphonate (aminosulphate). Nevertheless, 86 and 87.8 per cent. yields of the indicated quantity of the salt have been obtained, together with 78 and 85 per cent. of the full amount of nitrite as indicated by the urea method (p. 24). The production of such large quantities of the hydroxylaminetrisulphonate shows the inaccuracy of Claus's description of the changes concerned. According to that account, which is endorsed by Raschig, no nitrite is formed and the utmost yield of hydroxylaminetrisulphonate would be equivalent to only 75 per cent. of the sulphur of the hydroxylaminedisulphonate.

*Constitution.*—Strictly speaking, the product of the triacylation of hydroxylamine with sulphonate radicals can only be a disulphonate, the third sulphonate radical becoming sulphatic by its union with oxygen. But the name of hydroxylaminetrisulphonate is sufficiently appropriate for such a compound, since, although a sulphatic salt, it is not actually a sulphate, but a mixed anhydride of acid salts, one being the 2/3-normal hydroxylaminedisulphonate and the other the acid sulphate:



Lossen (*Ber.*, 1892, **25**, 440) has already pointed out that dibenzhydroxamic acid may be regarded as the mixed anhydride of benzhydroxamic acid and benzoic acid, and similarly in the case of other diacylhydroxylamines.\* Nitrososulphuric acid (nitrosyl hydrogen sulphate), the mixed anhydride of nitrous and sulphuric acids, is an example of a mixed inorganic anhydride. But the present salt, as the anhydride of two different acid salts, finds its close analogue in potassium hyponitrososulphate,  $(\text{SO}_3\text{K})\text{O}(\text{N}_2\text{OK})$  (Pelouze's 'nitrosulphate,' *Journ. Chem. Soc., Trans.*, 1885, **47**, 203, this *Journal*, **9**, 101, 277) which is the anhydride of acid hyponitrite and acid sulphate. The two mixed anhydrides agree in being stable in alkaline solution and unstable in acid solution, and in not giving barium sulphate with barium hydroxide or chloride.

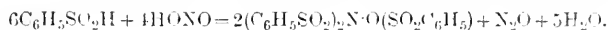
The evidence that the metasulphazilates have the constitution of hydroxylaminetrisulphonates is simple and direct, and similar to that as to the constitution of the hyponitrososulphates. In the first place, sodium amalgam decomposes them, apparently quantitatively (p. 26), into sulphate and normal aminedisulphonate (iminosulphate):—



no sulphite being formed. Instead of sodium amalgam, the zinc-copper couple may be used with the boiling solution to reduce hydroxylaminetrisulphonates (p. 28), but in this case the aminedisulphonate is apt to hydrolyse during the heating. The result of this reduction of the salts not only proves their sulphatic constitution but shows also that neither the formula,  $\text{ON}(\text{SO}_3\text{K})_2$  (Claus, Hantzsch), nor this formula doubled (Raschig) can possibly be right, because its

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\* Twenty-six years ago, Koenigs (*Ber.*, 1878, **11**, 615 and 1588) found that benzenesulphinic and nitrous acids react to form hydroxylaminedibenzsulphinic (dibenzsulphydroxamic) acid, and that this with more nitrous acid becomes a tribenzsulphinic compound. Preliminary experiments made for the author seem to show that the latter will almost certainly prove to be hydroxylaminetribenzsulphinic acid. Its production may probably be expressed by the following equation:—



acceptance would require that the sodium should act as a 'carrier' of oxygen to the sulphonate radical. Dunstan and Goulding (*Journ. Chem. Soc. Trans.*, 1899, **75**, 792) have found that trialkyloxamines, *e.g.*,  $(\text{CH}_3)_3\text{N}:\text{O}$ , are reduced to trialkylamines by zinc and acid. Were metasulphazilates also oxaminic in constitution, they too should be reduced to aminetrisulphonates (nitrilosulphates). Sulphites, and even sulphur dioxide have no action on the hydroxylaminetrisulphonates (p. 29).

In the second place, the metasulphazilates behave as sulphonated hydroxylamine. They reduce acidified permanganate; they give up one-third of their nitrogen in the form of ammonia when they are heated with soda-lime (Claus); and they can be hydrolysed ultimately into hydroxylamine and acid sulphate. Although very stable salts in other respects, they cannot, indeed, remain in solution very long or be kept for many months in the solid state without beginning to hydrolyse. But if a small amount of potassium or sodium hydroxide or, much more conveniently, of ammonia is added to their solution, they are permanent even for years in closed vessels. The other and less sulphonated hydroxylamines have no such stability, but always revert more or less to sulphite and either nitrite or nitrous oxide. The hydrolysis is expressed by the equation :



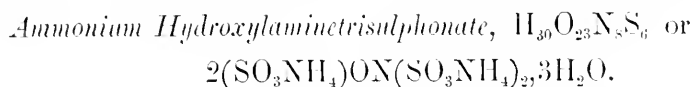
Taking into consideration their water of crystallisation, the potassium and the ammonium hydroxylaminetrisulphonates can only be written with doubled formulae, thus in some degree supporting Raschig's action in doubling Claus's formula for the former salt. But a cryoscopic measurement (p. 33) of the molecular magnitude of the sodium salt has shown that the simple formula is correct.

*Potassium Hydroxylaminetrisulphonate*,  $2(\text{SO}_3\text{K})\text{ON}(\text{SO}_3\text{K})_2 \cdot 3\text{H}_2\text{O}$ , hitherto the only known salt, occurs in flattened monosymmetric prisms, measurements of which have been made by Fock (Raschig).

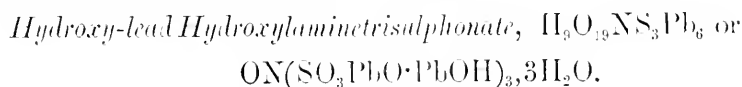
Its solubility in water at  $18^{\circ}$  is one in 25.37 parts. It is neutral to phenolphthalein, litmus, methyl-orange, and other indicators. When slowly heated to  $100-120^{\circ}$  in the air, it loses some of its water of crystallisation and is then hydrolysed by the remainder, acting together with the moisture of the atmosphere, so that at first it loses in weight and then gains. The residual mass is strongly acid owing to the presence of acid sulphate. It has not been found possible to avoid hydrolysis, even when the salt is very gradually heated in a current of dried air, after having already been exposed in a desiccator at the ordinary temperature. Its water, therefore, could only be determined by difference. As expressed in the foregoing formula, which agrees with Fremy's empirical formula, it is certainly  $3/2 \text{ H}_2\text{O}$ , although Claus made it out to be  $1/1 \text{ H}_2\text{O}$  only. In his paper, five concordant analyses of the anhydrous salt, besides four analyses of the hydrated salt, are given; and so far from reference being made to any difficulty being experienced in rendering the salt anhydrous, it is stated that the water of crystallisation easily escapes at  $100^{\circ}$ . But it is important to note that his four determinations of the water give numbers which are all somewhat higher than those required by his calculation, although the salt occurs in large, clear, non-deliquescent crystals, and that the figures thus calculated are but little if any higher than those obtained by the author in two direct determinations of loss of water by heating, in which the residues were always acid and therefore contained water. The salt has also been analysed by Raschig, but his results are not decisive one way or the other (p. 30).

*Sodium Hydroxylaminetrisulphonate*,  $(\text{SO}_3\text{Na})\text{ON}(\text{SO}_3\text{Na})_2, 2\text{H}_2\text{O}$ .—This salt, now prepared for the first time, is obtained by boiling a solution of  $2/3$ -normal sodium hydroxylaminedisulphonate and its equivalent half-molecule of sodium hydroxide with lead

peroxide. It is more difficult to purify from accompanying salts than the potassium salt, but by very cautious addition of sulphuric acid, these salts may be converted into sulphate, which can be easily separated from the hydroxylaminetrisulphonate by freezing. It crystallises in aggregates of small, tabular, monoclinic crystals (p. 31). The solubility of the salt is considerable, one part requiring only 2.83-2.85 parts of water at 21.5°. Like the potassium salt, it is neutral to indicators, and, when heated, hydrolyses in its water of crystallisation.



The analysis of this salt confirms the view that the amount of water present in the potassium salt is greater than that found by Claus. The ammonium salt forms thick, rhombic plates and prisms, similar to those of the potassium salt and probably isomorphous with them. But goniometric examination was impracticable, for although some faces were 7-9 mm. long, others were too imperfectly developed for determination. The salt is neutral to litmus and methyl-orange, and generally like the potassium salt, but it is exceedingly soluble in water, one part dissolving in 0.61 part at 16°. The salt examined was prepared by digesting the basic lead salt with ammonium carbonate and evaporating the solution on the water-bath until it had almost lost its alkalinity, and then concentrating it further under reduced pressure over solid potassium hydroxide. Its nitrogen and sulphur were found to be in much closer agreement with the formula showing 3/2 molecules of water; but here again the difference between the numbers for the two formulæ is not very great (p. 32).



This tetrabasic and very insoluble lead salt, which appears to be the only insoluble hydroxylaminetrisulphonate, was prepared by pouring

a warm solution of the potassium salt into excess of carefully prepared basic lead acetate solution. It is a chalky powder readily decomposed by a solution of an alkali carbonate (p. 32).

*Peroxyaminesulphonates*

(*sulphazilates ; oxysulphazotates ; nitroxydisulphonates*).

Only silver oxide and lead peroxide have, as yet, been used in the preparation of a peroxyaminesulphonate, but many other oxidising agents produce the violet coloration, thus indicating the conversion of a hydroxylaminedisulphonate into peroxyaminesulphonate, as was pointed out by Fremy; even chlorine when used in limited quantity is able to produce this change. Ozone is an excellent reagent, rapidly producing a strong solution of the peroxyaminesulphonate when it is passed into a faintly alkaline solution of the hydroxylaminedisulphonate. Nitrous fumes are absorbed by an ice-cold solution of this salt, which assumes a dark brown colour, and this solution, when rendered alkaline slowly acquires the violet colour of the peroxyaminesulphonate. Also, when an ice-cold solution of potassium hydroxylaminedisulphonate and nitrite is barely acidified, preferably with sulphur dioxide, similar effects are produced. The temporary production of a violet colour is frequently observed in experiments made with the compounds of potassium nitrite with potassium hydroxylaminedisulphonates (this Journ. **13**, 211). Hydrogen peroxide, potassium ferricyanide, potassium permanganate, and alkaline cupric solutions are all inactive with it. Even freshly precipitated mercuric oxide is without action upon it, although it is more quickly affected by light when it is suspended in a solution of the salt.

In preparing potassium peroxyaminesulphonate, Fremy showed a preference for the use of silver oxide, whilst Claus, who assumed that the action of silver oxide was apt to proceed too far, preferred lead peroxide. Silver oxide gives a somewhat better yield and



none of the silver goes into solution, whereas a little of the reduced lead peroxide dissolves and renders the salt impure. But the dissolved lead is readily removed and the lead peroxide presents the advantage of being at hand when wanted, whilst the silver oxide has to be prepared each time and the metal afterwards recovered. Lead peroxide has therefore been used in the present research.

Fremy used either the  $2/3$ - or the  $5/6$ -normal potassium hydroxylaminedisulphonate as the source of the peroxyaminesulphonate; Claus used only the latter, and Raschig chose the former. The advantage lies with the  $5/6$ -normal salt, for, when prepared from a less alkaline salt, the peroxyaminesulphonate proves to be less easily purified and consequently less stable. The  $5/6$ -normal salt is always so far hydrolysed in dissolving that it is converted into the  $2/3$ -normal salt, the potassium hydroxide being left in solution as noticed by Claus. The presence of free alkali, however, moderates the action of the oxidising agent, and to such an extent that a sufficiently concentrated solution of the very soluble normal sodium hydroxylaminedisulphonate is not attacked at all by lead peroxide. Apparently, therefore, lead peroxide acts as an acid oxidiser, in the form of plumbic anhydride, as suggested by Fremy.

The salt, which must be prepared just when it is wanted, is produced by mixing about 6 grams of the  $5/6$ -normal hydroxylaminedisulphonate (or the same amount of the  $2/3$ -normal salt together with a small quantity of a potassium hydroxide) and a little more than the same weight of lead peroxide (or of the silver oxide precipitated from a little less than the same weight of silver nitrate) and making up with water to 25 c.c. The mixture is agitated for 15 minutes in water near to, but not above,  $40^{\circ}$ . Then, the solution is decanted without delay, treated with carbon dioxide (when lead peroxide has been used), and filtered, before crystallisation sets in. The solution

should therefore be kept warm up to this point. When it has remained some hours in an ice-box, almost the whole of the peroxyaminesulphonate will have separated as a crust of minute orange yellow needles. These can be recrystallised, but not without material loss from hot water made slightly alkaline with potassium hydroxide. When, as appears to have been the case with Fremy, much hydroxylaminedisulphonate has been left unoxidised, some of this will be found with the peroxyaminesulphonate, from which it can hardly be wholly separated by recrystallisation, its crystals remaining coloured by the peroxyaminesulphonate, as observed by Hantzsch and Semple.

Any close determination of the yield cannot be made directly, since the salt can rarely even be roughly weighed before decomposition sets in. Its amount has, therefore, to be estimated by letting it decompose, igniting the residue with ammonium carbonate, and weighing the potassium sulphate. In this way the yield of separated salt was found to be a very little over three-fourths of the calculated quantity, when silver oxide was used; and a little less than two-thirds when lead peroxide was taken. But by indirect means, the amount of the salt actually produced can be shown to be much higher than this. As already mentioned (p. 5), the exhaustive oxidation by lead peroxide of a hot solution of hydroxylaminedisulphonate has given nearly 88 per cent. of the calculated quantity of hydroxylaminetrisulphonate, a fact which signifies that at least as much peroxyaminesulphonate as is equivalent to this percentage of the total sulphur must have been formed, since its production is intermediate to that of the hydroxylaminetrisulphonate.

Potassium peroxyaminesulphonate is very unstable in water and very little soluble in the cold. In N/10-solution of potassium hydroxide, which fairly represents its usual mother liquor, it is more stable, but still less soluble; 100 parts at 3° dissolve only 0.62 part

of the salt, and at 29° only 6.6 parts (p. 33). It interacts in solution with normal potassium sulphite and then produces hydroxylaminetrisulphonate and hydroxylaminedisulphonate, evidently in molecular proportions (p. 34), this change being a fact of great theoretical importance. Its chemical activity is manifested in oxidising certain easily oxidisable substances and being thereby reduced to its parent salt, hydroxylaminedisulphonate. Although it liberates iodine from hydroiodic acid, it fails to oxidise hydrochloric acid. When the latter acid in concentrated solution is poured upon the solid salt, it sets up the same decomposition as that which occurs spontaneously (p.15). But here, as the rise of temperature is moderated, definite although minute quantities of aminemonosulphonate and of hydroxylamine (not its sulphonate) can be found. The salt has practically no action on alcohol; nitrous and sulphurous acids rapidly reduce it, so also does sodium amalgam, first to hydroxylaminedisulphonate (as already observed by Schatzman), and then this salt passes slowly but completely into aminedisulphonate (iminosulphate). Clean granulated zinc slowly reduces the salt, but copper does not. The spontaneous decomposition of the salt may, however, easily be mistaken for its slow reduction by a reducing agent, since in this case also, as will be presently described (p. 16), hydroxylaminedisulphonate is produced. The difference is readily detected by testing for nitrite, which is produced only in the spontaneous decomposition of the salt. Manganese dioxide very slowly decomposes it, causing a minute effervescence; lead peroxide is inactive. Potassium permanganate is reduced to green manganate. Clean filter-paper, unlike the paper in use in Fremy's time, does not affect it.

Part of the instability of peroxyaminesulphonates must be attributed to the presence of oxidisable impurities. Thus, Fremy noticed the decomposing action of atmospheric dust; whilst nitrite, another impurity liable to be found in the salt, also greatly increas-

es its instability. Acids hasten the decomposition of the salt; alkalis retard it. When drained on the tile from an alkaline solution, the salt may, under cover, remain undecomposed for two hours or more; but if washed on the tile and thus deprived of the traces of its adherent alkaline mother liquor, it will decompose in a very few minutes. Nevertheless, on one occasion, some of the salt thus purified was kept on a tile for 11 months in a desiccator, and only then decomposed through an accident. This, however, must be regarded as a very uncommon experience. The sensitiveness of potassium peroxyaminesulphonate to acids has been recorded by others, but has been somewhat exaggerated. When the salt is free from every trace of nitrite, its cold acidified solution may remain coloured for 40 minutes. An alkaline solution may not lose all its colour when kept in a closed vessel for more than a month. If sufficiently pure, the solid salt may be preserved for a day or so under water rendered slightly alkaline with potassium hydroxide.

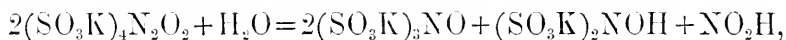
The nature of the decomposition of potassium peroxyamine-sulphonate occurring in the absence of alkali has already been examined, although in all cases very imperfectly, by Fremy and by Claus, and in the presence of alkali by Raschig. According to Fremy, the solid salt decomposes explosively when heated; when exposed to the air it becomes strongly acid; and when heated in solution it yields sulphate and a gas mistaken by him for oxygen, but which is really nitrous oxide. He was also mistaken in stating that it melts readily and that when left in a closed bottle it evolves nitric oxide. Claus found that, whether in the solid state or in solution, whether when cold or moderately heated, the decomposing salt yields hydroxyl-aminetrisulphonate and nitrous oxide, together with acid sulphate equivalent to one-fourth of its sulphur, according to the equation  $2K_4N_2S_4O_{14} + H_2O = 2KH_2SO_4 + 2K_3NS_3O_{10} + N_2O$ . Raschig has confirm-

ed Claus's statements and also states that the solid salt or its solution, also decomposes in this way even when left in contact with alkali. He also adds that its solution when acidified is decolorised in a few minutes, whilst in presence of alkali it can in some cases be heated to boiling without change. All these statements by Claus and Raschig require to be modified in order that they may accurately describe the behaviour of the salt, and even then they fail to indicate the primary change which the decomposing salt undergoes. Thus, the acid sulphate produced is seldom equal to one-fourth of the total sulphur, although it may be so, as twice found by Claus, and indeed also in the present investigation, but only when the salt had been used with too small a quantity of water to dissolve it all on warming. Owing to this fact, only a part of the nitrogen, which does not become hydroxylaminetrisulphonate, appears as nitrous oxide, along with a small amount of free nitrogen.

Solid potassium peroxyaminesulphonate is too unstable when dry and free from alkali, to exist many minutes without rapidly and almost explosively decomposing. In this decomposition, slight white fumes of ammonium salt (probably pyrosulphite and pyrosulphate), nitrogen and nitrous oxide, and a small quantity of sulphur dioxide are given off, whilst the residue, when the mass of the salt has been at all considerable, gets very hot (above  $300^{\circ}$ ?) and melts. This residue consists of potassium sulphate (principally pyrosulphate) with a very little ammonium salt. Sometimes a trace of aminemonosulphonate can be detected by the mercuric nitrate test; also a trace of hydroxylamine (or other substance reducing alkaline cupric solution), but none of the other sulphonates, the temperature having been too high to leave these substances undecomposed.

The true products of the spontaneous decomposition of a peroxyaminesulphonate are only found (in company with small

quantities of apparently secondary products) when the salt is heated to boiling with enough water to dissolve it, and in presence of sufficient alkali to prevent both the acidification of the solution during the decomposition of the salt and also the secondary changes which would result from acidification. The alkali does not appear to modify the nature of the primary change, although it distinctly increases the stability of the salt, as already mentioned (p. 14). When carried out in the foregoing manner, the decomposition of a peroxyaminesulphonate proceeds largely in such a way that not only do three-fourths of the sulphur of the salt, as suggested by Claus and by Raschig, together with one-half of its nitrogen, come out as hydroxylaminetrisulphonate, but the rest of the sulphur and one-fourth of the nitrogen become hydroxylaminedisulphonate again, whilst the remaining one-fourth of the nitrogen appears as nitrite,



although some nitrous oxide and sulphate, besides minute and uncertain quantities of other substances, are always produced (p. 20)

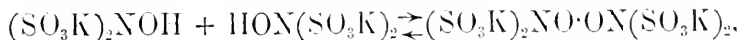
This result explains the production of the large quantities of acid sulphate and nitrous oxide observed by Claus and Raschig, for the nitrous acid when not neutralised by alkali interacts with the hydroxylaminedisulphonate and yields acid sulphate and nitrous oxide (this Journ., **13**, 212.)

The generation of hydroxylaminedisulphonate in the spontaneous decomposition of a peroxyaminesulphonate accounts for the fact, met with in the present investigation, that much more hydroxylaminetrisulphonate is obtainable by heating hydroxylaminedisulphonate in solution with excess of lead peroxide than can be derived from the decomposition (out of contact with lead peroxide) of the peroxyaminesulphonate equivalent to that quantity of hydroxylaminedisulphonate (p. 5). For in presence of lead peroxide, that hydroxyl-

aminedisulphonate which is regenerated by the independent decomposition of the peroxyaminesulphonate is oxidised again to more of this salt, to be again decomposed in the same way, until the whole of the disulphonate has become trisulphonate and nitrite, except that part of it which is lost as sulphate and nitrous oxide. Remembering that  $4(\text{SO}_3\text{K})_2\text{NOH}$  gives  $2(\text{SO}_3\text{K})_4\text{N}_2\text{O}_2$ , the larger yield of hydroxylaminetrisulphonate which should result will be seen, on comparing the equation on page 5 with that just given, to be theoretically as 4 to 3. It will now, too, be evident, on reference to Claus's memoir, that his incomplete knowledge of the nature of the decomposition of the peroxyaminesulphonate led him to object too much to Fremy's account of the action of the oxidising agent in producing hydroxylaminetrisulphonate.

*Constitution.*—The constitution of a peroxyaminesulphonate as a sulphonate was recognised by Claus, and is deducible from the fact that it is formed by the dehydrogenation of hydroxylaminedisulphonate. The problem of its constitution as a nitroxy-compound remains to be solved, and the description just given of the potassium salt amounts to a demonstration, first, that its constitution is that of a peroxide and therefore of a peroximide; and, secondly, that its nitrogen is trivalent.

Among the facts bearing on its constitution as a peroxyamine, that is, as a derivative of  $\text{H}_2\text{NO}\cdot\text{ONH}_2$ , are, first, those of its mode of formation. The  $2/3$ -normal hydroxylaminedisulphonate loses its two hydrogen atoms, at the ordinary temperature and when it is in aqueous solution, by the action of ozone, lead peroxide, silver oxide, and a variety of other substances:

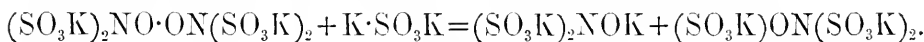


but not, however, by oxygen itself, for Raschig's observation, that a solution of hydroxylaminedisulphonate, when exposed to the air may

assume a slight violet colour, applies in reality only to the case where the 2/3-normal salt is contaminated with nitrite, the pure salt never oxidising nor colouring in this way. The interaction with lead peroxide points clearly either to the peroxide constitution or, but with much less probability, to a rise in the combining power of the nitrogen to quadrivalency.

The fact of the ready reversion, at the common temperature and in solution, of a peroxyaminesulphonate to a hydroxylaminedisulphonate by acting as an oxidising agent is equally strong evidence of the same constitution. This reversion is also quantitative to an extent that admits of its being used to estimate the amount of the salt present in a solution (Schatzmann, Hantzsch and Semple).

Its combination with a molecule of normal sulphite (p. 13) affords convincing evidence to the same effect, since it is effected through the oxygen atoms of the peroxyaminesulphonate :



This interaction will be again discussed on page 20. Inferentially in favour of the peroxide constitution are also the odour which the peroxyaminesulphonates impart to the skin, their colour, and their decomposition into nitrous acid and sulphonated hydroxylamines.

So soon as it is recognised that peroxyaminesulphonates are peroxides, all doubt is removed as to the valency of their nitrogen, which then can be only that of a triad. Contrariwise, when such a constitution is not admitted, the nitrogen of a peroxyaminesulphonate, with equal certainty, cannot be trivalent. In order, therefore, to strengthen the conviction that the peroxyaminesulphonates are indeed peroxides and peroximides, it becomes important to state the reasons against admitting the nitrogen of these salts to be quadrivalent or more than trivalent.

To begin with, it is extremely improbable that oxidation by



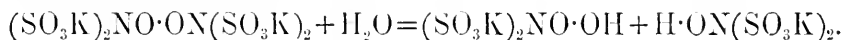
lead peroxide, silver oxide, or ozone should raise the valency of the nitrogen to only quadrivalency and not to quinquevalency, and that it should raise it at all without converting the sulphonate to sulphate radicals. Neither Claus nor Raschig assumes that it does, for according to them the nitrogen of the hydroxylaminedisulphonate is itself quinquevalent. But there are two strong reasons for rejecting the assumption that the valency of the nitrogen is raised by the oxidation of hydroxylaminedisulphonates to peroxyaminesulphonates. One of these is the nature of the products of the spontaneous decomposition of a peroxyaminesulphonate. These products, in so far as they contain nitrogen, are all trivalent nitrogen compounds, namely and in the main, hydroxylaminetrisulphonate, hydroxylaminedisulphonate, and nitrite; if nitrous oxide is also recognised, that will not affect the argument. No nitrate can be found among these products (p. 36). It is, of course, the establishment of the trivalency of the nitrogen of the first-named product which has really settled the matter. But as it is only as yet on the chemical work of Divers and the author (this Journ., 7, 34), that the adoption of the trivalency of the nitrogen in hydroxylaminedisulphonates can be based, the result of a determination by a cryoscopic method (p. 33) of the molecular magnitude of the normal sodium hydroxylaminedisulphonate may be adduced in support of it. This result shows that the molecule of the salt contains but one atom of nitrogen (necessarily therefore trivalent), and not two atoms as had been represented by Claus and by Raschig. Now, the spontaneous decomposition of a peroxyaminesulphonate can only be hydrolytic and, is therefore one not affecting the valency of the nitrogen; or, should this be contested, it can still be asserted that at least this decomposition cannot be interpreted as a change involving a fall of the valency of the nitrogen.

The other reason against the belief that the valency of the nitrogen changes when a hydroxylaminedisulphonate is oxidised to a peroxyaminesulphonate is that of the production of the two compounds of trivalent nitrogen, the hydroxylaminedisulphonate and hydroxylaminetrisulphonate by the union of a peroxyaminesulphonate with a normal sulphite (p. 13). These two reasons for regarding the nitrogen of a peroxyaminesulphonate as trivalent seem to be conclusive and therefore support the view that these salts are constituted as peroxides or peroximides.

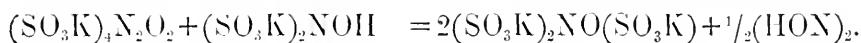
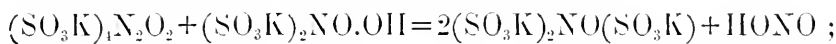
Since the sodium salt is even more unstable than the potassium salt, the determination of the molecular weight of a peroxyaminesulphonate has not been possible. It would seem better to modify Hantzsch and Semple's suggestion concerning the molecular weights of the two forms of the potassium salt (p. 3), to the extent of giving the simple formula,  $(\text{SO}_3\text{K})_4\text{N}_2\text{O}_2$ , to the violet form, and reserving the double formula, or even a higher multiple of this, for the yellow form.

*Products of Decomposition*—Without further experiments than those described on pages 23 and 41, the number of the products and the great variations in their proportions are such that the nature of the spontaneous decomposition of a peroxyaminesulphonate cannot yet be fully determined. But its general character can be indicated, now that the constitution of both peroxyaminesulphonates and hydroxylaminetrisulphonates has been determined.

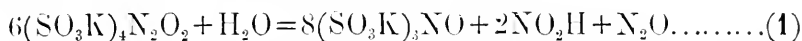
It can hardly be doubted that the molecule of peroxyaminesulphonate becomes halved by hydrolysis and converted into the hydroxylaminedisulphonate, always found in abundance, and the *hydroperoxylaminedisulphonate*, as yet undiscovered because incapable of continued existence, thus:



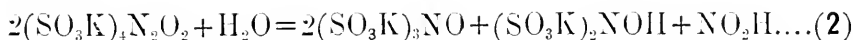
It is already known (this Journ **3**, 218 ; **7**, 40) that, in the presence of alkali, the nitroso-radicals of a hydroxylaminesulphonate tend to separate from the sulphonate radicals. Such a tendency, exercised in the presence of undecomposed peroxyaminesulphonate, will lead to the production of hydroxylaminetrisulphonate and nitrite in the case of hydroperoxyaminesulphonate, and of the former salt and hyponitrite in the case of hydroxylaminedisulphonate, thus :



When the three equations are combined, the intermediate products disappear and the following equation is left,



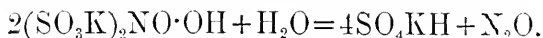
or, leaving the comparatively stable hydroxylaminedisulphonate unchanged,



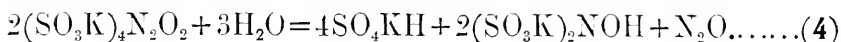
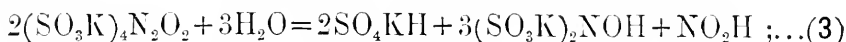
It is fairly certain that the sulphate which, in greatly varying although never very large quantity, is always produced, does not come from the hydrolysis of the salt itself or from that of either the hydroxylaminetrisulphonate or hydroxylaminedisulphonate derived from it. For the trisulphonate is remarkably stable in presence of alkali, and the disulphonate, although unstable in its presence, yields not sulphate but sulphite. As this is also true of hydroxylaminemonosulphonate, it may be assumed to be so in the case of peroxyaminesulphonate. The sulphate should therefore have another origin, which may well be taken to be the decomposition of the hydroperoxyaminesulphonate in circumstances in which it fails to interact with peroxyaminesulphonate, perhaps because the temperature of the solution is too low. In that case, it will naturally hydrolyse, one half becoming hydroxylaminedisulphonate by oxidising the other half into sulphate and nitrous acid,



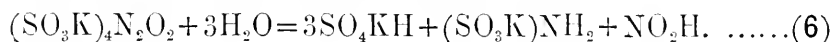
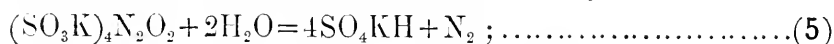
Or, it may well hydrolyse wholly into sulphate and nitrous oxide,



These equations combined with the primary equation give,



An equation to account for the production of nitrogen, and another for that of aminemonosulphonate are easily framed :



A justification of the lower of these equations and an illustration of the nature of the change expressed by it are to be found in the production of aminemonosulphonate from hydroxylaminedisulphonate when decomposing in presence of copper sulphate (this Journ., **13** 497).

By combining these six equations in different ways, the various results obtained can be explained (p. 42), although the conditions for the occurrence of one mode of decomposition more than another are not yet ascertained.

*Sabatier's Bluish-violet Acid.*—Sabatier has studied the nature of the bluish-violet colour produced in a solution of nitrososulphuric acid (nitrosyl hydrogen sulphate) in the monohydrate of sulphuric acid by sulphur dioxide, and in other ways (*loc. cit.* p. 3); and has found this colour to be more closely like that of a solution of potassium sulphazilate than the colour of the latter is like that of a solution of potassium permanganate. On this ground and from a consideration of the circumstances which give rise to it, he has suggested that it is due to the presence in the solution of the acid of Fremy's salt, constituted according to the formula,  $\text{ON}(\text{SO}_3\text{H})_2$ . Sabatier may be right, but there is much to be said against this opinion. Firstly, the tints of the two coloured solutions are not so

similar as he asserts. Secondly, certain striking contrasts may be observed in the chemical character of the two solutions. Potassium peroxyaminesulphonate is produced by the action of lead peroxide and is not attacked by it, whereas the coloured acid solution is at once oxidised by lead peroxide. Conversely, whilst this acid solution is indifferent towards sulphur dioxide and produced by it, potassium peroxyaminesulphonate is at once changed by this reagent.

Then, again, it has not proved to be possible to convert potassium peroxyaminesulphonate into this violet acid solution or to effect the opposite change. Mr. S. Sekiguchi, a Post-graduate of this University, has kindly carried out some experiments in this direction. Making the mixtures very gradually and keeping them cold by ice and salt, he has poured the solution, prepared from nitrososulphuric acid and sulphur dioxide in sulphuric acid, into a solution of potassium hydroxide ; and, on the other hand, an aqueous solution of potassium peroxyaminesulphonate into some concentrated sulphuric acid ; in both cases, an almost immediate disappearance of the violet colour results. In the former case, too, the alkaline solution was evaporated and crystallised, without finding any of the hydroxylaminetrisulphonate which would result from the decomposition of peroxyaminesulphonic acid and might, to some extent, in accordance with its usual stability, escape decomposition.

#### *Details of Experiments.*

##### *The Exhaustive Action of Lead Peroxide on Hydroxylaminesulphonates.*

2/3-normal potassium hydroxylaminedisulphonate was boiled with excess of lead peroxide in about 15 times its weight of water, containing from 1/5 to 2/5 of a molecule of potassium hydroxide, until the solution had again become colourless. To the cold filtrate, just enough barium acetate was added to precipitate all sulphate

present ; the filtrate was then evaporated, and the hydroxylaminetrisulphonate crystallised out as far as possible and weighed. Potassium nitrite, produced in large quantity, was estimated in the mother liquor and alcoholic washings of the crystals of the hydroxylaminetrisulphonate by the urea method. Sulphate was found partly in solution and partly in the lead residue, which was extracted alternately with dilute nitric acid and potassium hydroxide. The sulphate, both in solution and residue, was estimated and, in two cases, the soluble lead also, as a measure of lead peroxide consumed.

In one experiment, 73.2 grams of salt gave 58.2 grams of trisulphonate in crystals, that is, 58.5 mol. of trisulphonate from 100 mol. of disulphonate, or 87.75 per cent. of the theoretical quantity. Nothing else was determined, and so high a yield of hydroxylamine-trisulphonate was only reached by adding alcohol to separate the last portions of the salt from the very concentrated nitrite mother liquor.

In another experiment, 125 grams of the disulphonate gave 97.33 grams of trisulphonate, equal to 57.33 mol. of trisulphonate to 100 mol. of disulphonate, or 86 per cent. of the calculated quantity. The amount of potassium sulphate was 21.5 mol. per 100 mol. of salt taken, which leaves sulphur for the trisulphonate equivalent to 59.5 mol., as against the 57.33 mol. of crystallised salt. Very much nitrite was found, 37.5 mol. per 100 mol. of disulphonate taken, indicating the production of very little nitrous oxide. The only way to interpret this large production of nitrite is to assume that, whilst 89.25 per cent. of the salt was oxidised into trisulphonate and nitrite, and only 3 per cent. into sulphate and nitrous oxide, 7.75 per cent. was oxidised into sulphate and nitrite, an assumption which cannot be easily justified.

In an earlier experiment, in which the crystallisation of the

trisulphonate was only imperfectly carried out, 136.33 grams of the disulphonate gave 84.33 grams of the crystalline product that is, 100 mol. gave 45.56 mol., or 68.33 per cent. of the theoretical quantity. But, since the quantity of sulphate, almost if not actually the only other sulphur compound produced, amounted to only 19 mol. per 100 of disulphonate, the actual yield of trisulphonate can have been little short of 60.33 mol. per 100. The nitrite, as determined by the urea method, was 28.4 mol. per 100 of disulphonate taken. But the lead peroxide consumed was in this case determined, and made out to be 71.5 mol. per 100 mol. disulphonate, and this indicates the production of 31.8 mol. nitrite. Accepting the mean of these numbers for the nitrite, it results that about 90 per cent. of the hydroxylaminedisulphonate was converted into trisulphonate and nitrite, and the rest into sulphate and nitrous oxide.

In an experiment with 35 grams of potassium hydroxylamine-disulphonate, in which the crystals of hydroxylaminetrisulphonate were not weighed, 100 mol. yielded 13 mol. of sulphate and 26 mol. of nitrite. Calculating from these quantities, 78 per cent. of the salt was oxidised into trisulphonate and nitrite, 15.5 into trisulphonate and nitrous oxide, and 6.5 into sulphate and nitrous oxide. The trisulphonate produced will therefore have been about 93.5 per cent. of the calculated quantity, or 62.33 mol. per 100 mol. disulphonate.

Another experiment was made on the normal sodium hydroxylaminedisulphonate (this Journ. 7, 49) in dilute solution, 11.33 grams being taken without adding sodium hydroxide, because the alkalinity of the salt was sufficient to protect it. But in this experiment, only the quantities of lead peroxide consumed and of sulphate formed were estimated. Exactly as happened in the

experiment with the potassium salt, 71.5 mol. of lead peroxide were consumed per 100 mol. sodium salt. The sulphate amounted to 34 mol. per 100 mol. of salt used, more, that is, than in the experiments with the potassium salt. The calculated quantity of sodium hydroxylaminetrisulphonate was correspondingly lower, 55 mol. per 100 mol. or 82.75 per cent. of the theoretically possible quantity.

*Reduction of Potassium Hydroxylaminetrisulphonate by Sodium Amalgam.*—In the interaction between sodium amalgam and potassium hydroxylaminetrisulphonate in aqueous solution, the two liquids become warm and the action is soon over, if the two are well shaken together. No gas is evolved, and nothing is left in solution but the two salts, sulphate and aminedisulphonate (iminosulphate). The latter is easily recognisable by its separating as the very sparingly soluble  $2/3$ -normal potassium salt when the solution is nearly neutralised with an acid, and also by its nearly insoluble normal mercury-potassium salt (this Journ. 6, 96 ; 9, 210). But the salt was also analysed quantitatively (p. 28) in order to demonstrate its nature beyond question. By cautiously adding hydrochloric acid to the cold solution until it has become almost neutral to methyl-orange and then precipitating with barium chloride, the sulphate is partially separable from the aminedisulphonate. The latter may then be estimated as sulphate in the filtrate after hydrolysis at  $150^{\circ}$ . In an experiment carried out in this way upon 2.447 grams of potassium hydroxylaminetrisulphonate, the barium sulphate was washed with cold and then with hot water, ignited, and weighed. The sulphate from the hydrolysed aminedisulphonate was treated as in an ordinary sulphate determination. In this way determined, 34.79 per cent. of the sulphur came out as sulphate and 64.88 per cent. as aminedisulphonate, leaving 0.33 per cent. unaccounted for. In



accordance with the equation, the actual numbers should have been 33.33 and 66.67 per cent. respectively. By other experiments it was, however, established that some of the aminedisulphonate was precipitated with the sulphate. No doubt, also, some barium chloride was carried down.

Potassium hydroxylaminetrisulphonate, 1.441 grams, was reduced by sodium amalgam, and the solution neutralised and precipitated in the cold by barium chloride as above described. The washed precipitate was then heated for four hours at  $150^{\circ}$  with dilute hydrochloric acid in a sealed tube. The acid was nearly neutralised, and the barium sulphate collected, washed, and weighed as usual. The filtrate from this yielded a fresh precipitate with barium chloride, for the barium aminedisulphonate, which was precipitated with the sulphate, had been hydrolysed into barium sulphate and ammonium hydrogen sulphate. Therefore, from the weight of the main precipitate of sulphate was deducted that of the small quantity last obtained, and the remainder taken as sulphate actually produced by the sodium reduction. It amounted to the equivalent of 34.20 per cent. of the total sulphur. The aminedisulphonate in the original filtrate from crude sulphate was determined by hydrolysing and weighing its sulphur as sulphate. To the weight of this was added twice that of the barium sulphate obtained, as just described, from the soluble sulphate extracted by hydrolysing the crude barium sulphate, because twice that quantity represented the total sulphur of the aminedisulphonate precipitated along with the sulphate. This sum was equivalent to 65.75 per cent. of the total sulphur. That these data still deviate from the calculated numbers is no doubt due to the adsorption of a little barium chloride to the sulphate when precipitated in the cold. The barium of this chloride will have

rendered insoluble some of the sulphate which should have dissolved out through the hydrolysis of the aminedisulphonate simultaneously precipitated. There seems, therefore, to be no reason for doubting the quantitative accuracy of the equation given on page 6.

An experiment was then tried to see whether closer results could not be got by removing as much as possible of the aminedisulphonate from the solution before precipitating the sulphate, first crystallising out most of it from the nearly neutralised solution, and then removing some of the remainder as the mercury-potassium salt, by digesting the solution with mercuric oxide. This method, however, did not give better results than the preceding.

*Reduction of Potassium Hydroxylaminetrisulphonate by the Zinc-copper Couple.*—The reduction of the trisulphonate was successfully effected by boiling its solution, (to which a few drops of solution of sodium acetate had been added in order to protect the salt from hydrolysis) with some zinc-copper couple. But in consequence of the necessity of boiling the solution, hydrolysis of the aminedisulphonate is apt to set in.

Some aminedisulphonate, prepared by the sodium amalgam method and another sample, prepared by the zinc-copper couple were analysed with the following results :

	By sodium.	By zinc-copper.	Calc.
Potassium	30.68	30.72 ———	30.89
Sulphur	25.09	24.85    25.94	25.30
Nitrogen	5.32	6.16	5.54

*Hydrolysis of a Hydroxylaminetrisulphonate.*—The complete hydrolysis of the hydroxylaminetrisulphonates is more difficult to effect than that of any other of Fremy's salts. In the quantitative analysis of the salts, it was found necessary to keep the acidified solution for five hours at 180—200°. In the case of the potassium salt, the mean percentage of sulphur then came out as 23.18 ; at

150° only, for four hours, it was 22·85; and at 90—100° for five hours and then three hours at 130°, it gave only 22·64. In this case, the nitrogen of the hydroxylamine obtained (as measured by the iodine method) amounted only to 2·5 per cent. In another case, where the hydrolysis was allowed to go on for 48 hours at 90-95° and then 2 hours at 130-134°, the nitrogen obtained as hydroxylamine was 2·71 per cent. (79·75 per cent. of total nitrogen).

*Inactivity of Sulphites towards Hydroxylaminetrisulphonates.*—Potassium hydroxylaminetrisulphonate weighing 2 grams, in sufficient water to keep the salt in solution, was left for 3 days with 3 grams of potassium metasulphite, rendered slightly alkaline to lacmoid paper (whilst strongly acid to litmus). The sulphite was then precipitated by barium hydroxide and the filtrate evaporated. In this way 1·98 grams of the hydroxylaminetrisulphonate were crystallised out. The analysis of the salt thus recovered is given as that of II among the analyses of the salt below.

*Analysis of Potassium Hydroxylaminetrisulphonate.*—Although this has been analysed by previous workers, it was necessary to make several careful and full analyses in order to establish the fact that it contains more water of crystallisation than the proportion stated by Claus and by Raschig. Four separate preparations were analysed.

I. 0·4954 g. substance gave 0·3117 g. potassium sulphate; 0·5688g. gave 0·8581g. barium sulphate; 0·3387g. gave 0·5680g. barium sulphate; 0·2821g. substance, finely powdered and heated in a current of dried air, first at 95° and then up to 110°, lost 0·0138g.; 0·2174g. lost in this way 0·0101g.

II. 0·2272g. substance gave 0·1429g. potassium sulphate; 1·0676g. treated with sodium amalgam for 24 hours and then hydrolysed at 150° for 3 hours, gave 1·7918g. barium sulphate and ammonia=25·59c.c. N/10 acid.

III. 0.2288g. substance gave 0.1451g. potassium sulphate ; 0.1003g. gave 0.1710g. barium sulphate.

IV. 0.8505g. substance gave 0.5347g. potassium sulphate ; 0.34475g. gave 0.5799g. barium sulphate ; 2.4425g. by sodium amalgam treatment and hydrolysis at  $150^{\circ}$  for 3 hours, gave ammonia=51.38c.c. N/10 acid ; 0.7650g. by the Dumas method gave 22.3c.c moist nitrogen at  $16^{\circ}$  and 758mm.

	Potassium.	Sulphur.	Nitrogen.	Water.
Found :				
I.,	28.25	$\left\{ \begin{array}{l} 23.18 \\ 23.05 \end{array} \right.$	—	(4.89) (4.65)
„ II.,	28.24	23.07	3.37	—
„ III.,	28.47	23.42	—	—
„ IV.,	28.23	23.12	$\left\{ \begin{array}{l} (2.95) \\ 3.39 \end{array} \right.$	— —
Meaa,	28.30	23.18	3.38	(4.77)
Calc. for $1/1$ $H_2O$ ,	28.95	23.71	3.46	4.49
„ $3/2$ $H_2O$ ,	28.32	23.19	3.39	6.52
Fremy,	28.02	23.40	3.48	—
Claus, found (taking old at opnic. weights.)				
	28.63	—	3.24	5.04
„ „ „	28.55	—	—	5.20
„ „ „	28.67	23.69	—	5.01
„ „ „	28.79	23.76	3.31	4.71
Claus, mean,	28.66	23.73	3.28	4.99
„ calc. (old at. wts.),	28.88	23.70	3.45	4.44
Raschig,	28.47	23.64	—	—
„	28.54	23.38	—	—

Claus has also given the results of five closely concordant analyses of the anhydrous salt, and should therefore have experienced no difficulty in rendering it anhydrous. In the attempts to deter-

mine total water, recorded above, the residue was always acid in consequence of unavoidable hydrolysis and fixation of some of the water of crystallisation. A discussion of this matter is given on page 8.

*Analysis of the Sodium Salt.*—Two distinct preparations of the sodium salt were analysed :

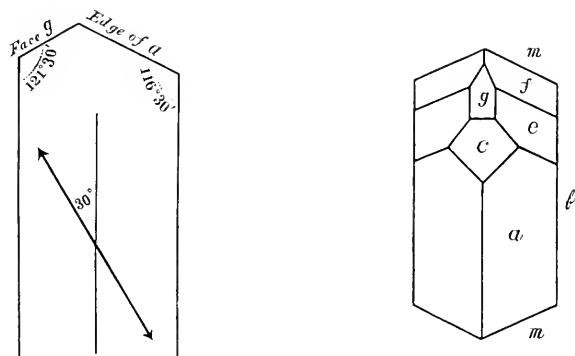
I. 0.4910 g. substance gave 0.2801 g. sodium sulphate ; 0.3845 g. gave 0.7174 g. barium sulphate, after hydrolysis at  $200^{\circ}$  for 3 hours. Hydrolysed at only  $160^{\circ}$  for 5 hours, 0.4548 g. gave 0.8378 g. barium sulphate, = sulphur 25.30 per cent. only.

II. 0.6097 g. substance gave 0.3455 g. sodium sulphate ; 0.1750 g. gave 0.3268 g. barium sulphate, after hydrolysis at  $210^{\circ}$  for 3 hours ; 0.7533 g. gave 24.0 c.c. moist nitrogen at 760.8 mm. and  $17^{\circ}$ , = 0.0279 g. nitrogen.

	Sodium.	Sulphur.	Nitrogen.
Found, I.,	18.50	25.64	—
„ II.,	18.36	25.67	3.70
$\text{Na}_3\text{S}_3\text{NO}_{10}, 2\text{H}_2\text{O}$ ,	18.42	25.62	3.76

*Crystallography of Sodium Hydroxylaminetrisulphonate.*—Professor Jimbō has kindly given me the following description of the crystals of this salt, which were examined under his directions by Mr. Y. Ōtsuki, University Post-graduate. Thick, tabular, monoclinic crystals, about 3 mm. long and 2 mm. wide, elongated in the direction of the vertical axis. The observed faces are of seven kinds, of which  $b$  is the largest and apparently the plane of symmetry.  $m$ , making with  $b$  an angle of about  $115^{\circ}$ , may be taken as a prism ;  $d$ ,  $e$ , and  $f$  as pyramids ;  $c$  as the base, and  $g$  as a positive orthodome. Two other faces in the zone of the orthodiagonal are sometimes observed. A crystal laid flat on the clinopinacoid shows an

extinction angle of  $30^\circ$  to the vertical axis, in the acute angle between this and the clinodiagonal.



*Analysis of the Ammonium Salt.*—

0.3005 g. substance gave 0.6045 g. barium sulphate, after hydrolysis at  $195^\circ$  for 5 hours; 0.1207 g. gave 16.57 c.c. moist nitrogen at 763 mm. and  $15^\circ$  C.

	Found.	$2\text{H}_{12}\text{O}_{10}\text{N}_4\text{S}_3 \cdot 3\text{H}_2\text{O}$	$\text{H}_{12}\text{O}_{10}\text{N}_4\text{S}_3\text{H}_2\text{O}$
Sulphur	27.63	27.36	28.08
Nitrogen	16.06	15.98	16.40

*Analysis of the Basic Lead Salt.*—The salt was dried for analysis in a current of dried air at  $100^\circ$  in the case of preparation I, and at  $110^\circ$  in that of II. The salt was quite free from potassium but contained a trace of acetate.

I. 0.4441 g. substance gave 0.3560 g. lead oxide and 0.1936 g. barium sulphate.

II. 0.3775 g. substance gave 0.4098 g. lead sulphate.

		Found.	Found.	$\text{O}_{16}\text{NS}_3\text{Pb}_6 \cdot 3\text{H}_2\text{O}$
Lead	I.	74.41	II. 74.14	74.71
Sulphur		5.99	—	5.79

*Determination of the Molecular Magnitude of Sodium Hydroxylamine-trisulphonate.*—This was carried out by Löwenherz's method with melted sodium sulphate crystals (*Zeit. physikal. Chem.*, 1896, **18**, 70) and using hydrated sodium hydroxylaminetrisulphonate. Sodium sulphate gets by dissolution in it of the hydrated hydroxylamine-trisulphonate a little more water than corresponds to the hydrate with 10 molecules of water, but the crystalline sulphate separates the anhydrous salt in abundance on fusion, and as the crystallising temperature of the melted salt does not change as long as the anhydrous salt remains at the bottom, this additional water is only equivalent to the use of a slightly greater quantity of the crystallised salt. A correction was, therefore, introduced by calculating from this additional water the corresponding quantity of hydrated sodium sulphate.

Hydrated salt	Anhydrous salt	Glauber's salt taken.	Glauber's salt corrected	$\Delta t$	M. W.
$O_1NS_3Na_3 \cdot 2H_2O$					
2.479g	2.2411g	58.985g	59.411g	0.369°	332.2
3.3417g	3.0210g	56.946g	57.520g	0.510°	335.6
$O_{10}NS_3Na_3$ requires 339.4					

*Molecular Magnitude of Normal Sodium Hydroxylaminedisulphonate.*

Hydrated salt.	Anhydrous salt.	Glauber's salt taken.	Glauber's salt corrected.	$\Delta t$	M. W.
$N_aON(SO_3Na)_2 \cdot 3H_2O$					
1.2200g	1.0093g	36.818g	37.198g	0.39°	233.2
2.4455g	2.0230g	36.442g	37.198g	0.74°	239.6
$O_7NS_2Na_3$ requires 259.3					

*Solubility of Peroxylaminesulphonate in N/10 Solution of Potassium Hydroxide.*—The purified salt, previously washed on the porous tile with some of the solvent, was shaken with it for from 15 to 20 minutes, the temperature of the solution being 29°. After some time 5 c.c. of the clear solution were pipetted off. The rest of the solution, along with the undissolved salt, was left for some hours in ice, when

again 5 c.c. were taken out, the temperature being then 3°. The two portions were each weighed and the amount of dissolved salt ascertained by a sulphur determination. It was thus found that 0.163 gram of salt was dissolved in 5.03 grams of its alkaline solution at 29°, and that 0.027 gram was dissolved in 4.98 grams of its solution at 3°.

*Interaction of Potassium Peroxylaminesulphonate and Normal Potassium Sulphite*.—To a solution of 3.6 grams of potassium peroxylamine-sulphonate, containing a very small quantity of potassium hydroxide, a solution of normal potassium sulphite (neutral to phenolphthalein) was added from a burette, with constant stirring, until the violet colour of the solution was entirely discharged. The change took place quickly but not instantly. The quantity of sulphite required was only a little more than that indicated by theory. After a short interval, baryta water was added to precipitate the excess of sulphite and the hydroxylaminedisulphonate. The excess of baryta was removed from the filtered solution by carbon dioxide and the filtered solution evaporated so as to get out as much as possible of the sparingly soluble potassium hydroxylaminetrisulphonate. Some more of this salt was precipitated by adding twice the volume of alcohol and leaving the mixture for some time. The total trisulphonate thus separated weighed 2.268 grams, or 81.5 per cent. of the calculated quantity.

The barium precipitate was triturated in a mortar with very dilute acetic acid, added very slowly so as to avoid as far as possible having any local excess of acid. When the solution had become neutral to phenolphthalein, the undissolved barium sulphite was filtered off. Potassium carbonate in slight excess was added and the whole left to stand for a day. Then, the solution, filtered from the barium carbonate and neutralised with acetic acid, was concentrated in a vacuum over sulphuric acid and mixed with twice its volume of alcohol. In 12 hours, the quantity of precipitated crystalline 2/3-



normal hydroxylaminedisulphonate weighed 1.55 grams, this being equal to 76 per cent. of the calculated quantity. It was pure, except for a trace of aminetrisulphonate (nitrilosulphate), doubtless due to the action of the sulphurous acid unavoidably liberated in the process of separating the barium sulphite from its own barium salt by acetic acid. It was identified by hydrolysis into sulphate and hydroxylaminemonosulphonate, and above all by its producing the bluish-violet peroxylaminesulphonate when warmed with lead peroxide and a small quantity of alkali. No nitrite was found in the mother liquor of the hydroxylaminetrisulphonate, showing that the production of the latter salt had not been due to spontaneous decomposition of the peroxylaminesulphonate. Hydroxylaminetrisulphonate and disulphonate are, in fact, the only substances which could be detected among the products of the interaction of the peroxylaminesulphonate and sulphite. Since, therefore, the separated quantities of these products were found to be in approximately molecular proportions, and as these salts are not insoluble, even in their alcoholic mother liquors, it may be regarded as proved that the interaction which takes place is exclusively that represented by the equation on page 18.

*Spontaneous Decomposition of Potassium Peroxylaminesulphonate.*—The principal products of the spontaneous decomposition of a peroxyaminedisulphonate in hot alkaline solution are easy to recognise. Unless very dilute, the solution yields crystals on cooling and more on evaporation. At first the sparingly soluble hydroxylaminetrisulphonate alone crystallises, and later on both this and the equally sparingly soluble hydroxylaminedisulphonate. In each case the crystals are characteristic and easily distinguished. The presence of the disulphonate in the solution is quickly and distinctively indicated, as has just been mentioned, by warming with a small quantity of

lead peroxide, which gives it again the bluish-violet colour of peroxy-aminosulphonate. By removing sulphate and hydroxylaminedisulphonate from the solution by barium hydroxide, nearly all the hydroxylaminetrisulphonate can be crystallised out; the mother liquor containing the nitrite may then be tested in any of the usual ways for this salt.

It was important to know whether any nitrate is formed by the decomposition, and therefore necessary first to get rid of all the nitrite present by a process that does not convert any of it into nitrate. The nitrite was accordingly changed into aminetrisulphonate (nitrilosulphate) by adding enough potassium carbonate and then passing in sulphur dioxide until the solution became acid, at which point the aminetrisulphonate that had been produced at once hydrolysed (this Journal 6, 65). Lastly, by blowing in air until all the remaining sulphur dioxide had been expelled, the acid solution was left free from either nitrite or sulphite, and, therefore, ready for testing for nitrate. None of this salt was found. The application of the process of sulphonating the nitrite to the determination of total nitrogen in solution, is described on page 39).

The testing for aminemonosulphonate (aminosulphate) among the products of decomposition of a peroxyaminosulphonate is not an easy matter. The method adopted was to oxidise all the hydroxylaminedisulphonate by boiling the solution with lead peroxide until it was again colourless. The nitrite was then oxidised by pouring the solution into potassium permanganate solution to which sulphuric acid had been added. Mercuric nitrate solution then precipitated from it a little oxymercuric aminemonosulphonate (this Journal, 9, 242), which, when treated with hydrogen sulphide, left the acid again in solution. By evaporation and addition of strong sulphuric acid,

the acid was obtained in characteristic crystals (*loc. cit.*, 229), which were sometimes weighed.

The quantitative examination of the solution is a troublesome and less satisfactory operation. The peroxyaminesulphonate can hardly be obtained for weighing in the dry and pure state, because of its instability. Therefore, after its composition had been found, from concordant analyses of four different preparations, to be that ascertained by previous workers, the preparation of the solution and its analysis after the salt had all decomposed were carried out in the following way. The peroxyaminesulphonate, recrystallised two or three times from hot water made alkaline with potassium hydroxide, was drained a short time on a tile from its mother liquor, and at once dissolved in suitable quantity in water to which had been added a measured quantity of potassium hydroxide. The solution was maintained at the boiling temperature until colourless through the complete decomposition of the salt. The cold solution was weighed off into four portions; one of 5 per cent. of the whole, for estimating the amount of peroxyaminesulphonate that had been dissolved; another of 15 per cent., for estimating the quantity of hydroxylamine-trisulphonate produced; a third and a fourth portion, each of 40 per cent., for estimating in one the quantity of sulphate and in the other that of nitrite produced. The quantity of peroxyaminesulphonate taken was determined by weighing as barium sulphate the total sulphur in the solution. To ensure the hydrolysis of all the sulphonate, the solution was heated with the hydrochloric acid in sealed tubes for 4-5 hours at 180°-200°.

To determine the quantity of sulphate which had been produced, very dilute hydrochloric acid was added with constant stirring until the solution was left only barely alkaline to phenolphthalein, then much ammonium chloride was added before precipitating with

barium chloride, in order to keep the hydroxylaminedisulphonate in solution as far as possible. The impure sulphate, washed with ammonium chloride solution on the filter, was transferred to a beaker and digested in the cold with very dilute hydrochloric acid, washed again on the filter with boiling water, and then ignited in the usual way.

The hydroxylaminetrisulphonate was estimated by leaving the solution with sodium amalgam for two days, occasionally shaking the two together, so as to convert this salt into hydroxylaminedisulphonate, and then all the hydroxylaminedisulphonate in the solution into aminedisulphonate (iminosulphate). The mercury having been filtered off and washed, hydrochloric acid was added to the solution until it was only just alkaline to methyl-orange, and then an excess of ammonium chloride was introduced. The sulphate was finally precipitated and treated as before described. Deducting from this quantity of sulphate that which was present before the treatment with sodium amalgam, there remained the sulphate equivalent to one-third of the sulphur of the hydroxylaminetrisulphonate, from which the quantity of this salt was calculated. Assuming hydroxylaminedisulphonate to be the only other sulphur compound produced in the decomposition of the peroxyaminesulphonate—an assumption nearly exact—the amount of this salt was then calculated as being equivalent to the sulphur not found either as sulphate or hydroxylaminetrisulphonate. The slight error in this assumption is caused by the production of very small quantities of aminemonosulphonate (aminosulphate). As to the last-named salt, it has not been possible to do more than ascertain that its quantity is usually quite small, although 2 mol. of the crystalline acid (p. 36) per 100 mol. of hydroxylaminedisulphonate oxidised by the lead peroxide were once actually obtained. In other words, the amount of the sulphur found as aminemono-

sulphonate was in this instance 1.03 per cent. of that of the hydroxylaminedisulphonate used.

To determine the total nitrogen in the solution, the nitrite was completely sulphonated to aminetrisulphonate (nitrilosulphate) by adding enough potassium carbonate for the purpose and then passing in sulphur dioxide until a piece of lacmoid-paper was just reddened (this Journ., **6**, 65). Next, the hydroxylaminetrisulphonate in the solution was reduced by sodium amalgam, as above described, to sulphate and aminedisulphonate. Having thus brought all the nitrogen to the state of aminesulphonates, the hydrolysis of these substances by hydrochloric acid was effected by heating, first, on the water-bath until all the sulphur dioxide had been expelled, and then for some hours in a pressure-tube at 150°. The solution distilled with alkali gave up all its nitrogen as ammonia. The difference between this and that originally present as peroxyaminesulphonate gives, indirectly, the quantity of nitrogen in the gases, whilst the difference, again, between the total nitrogen in the solution and the sum of the quantities found as disulphonate and trisulphonate is the nitrogen which was present as nitrite.

Although the experimental work in estimating sulphate and hydroxylaminetrisulphonate was performed with great care, no high degree of accuracy in the results could be expected. A test experiment was made to see to what extent the method was imperfect. A solution was prepared by dissolving potassium sulphate, potassium hydroxylaminetrisulphonate, potassium hydroxylaminedisulphonate, and sodium nitrite in water to every 100 c.c. of which 5 c.c. of N/10 solution of potassium hydroxide had been added. The solution was twice analysed for sulphate and trisulphonate, in the way described above. The quantities, taken and found, are here given in grams per 100 c.c.

	Taken.	Found.	
Trisulphonate,	2.580	2.547	2.624
Sulphate,	.347	.380	.373
Disulphonate,	.622	.629	.551
Nitrite,	.208	.212	.217

From this experiment, it seems that the sulphate may come out nearly 10 per cent. too high, no doubt for two reasons; one that, being precipitated in the cold, the barium sulphate retained other salts with it; the other and principal reason being that, in the process of neutralising the solution, some of the disulphonate must be decomposed, yielding sulphate. The numbers for the trisulphonate are much more satisfactory, being less than 1.7 per cent. too high, apparently because they represent the difference between two sulphate determinations, the error in the one counterbalancing the corresponding error in the other. When, however, we come to the numbers for the disulphonate, which are calculated from those for the other substances, it is seen how large the error may become, being in one case as much as 11.4 per cent. too low. Similarly, the quantity of nitrite calculated from those of the other substances may come out as much as 4.5 per cent. too high. The expression of the errors as percentages only holds good, of course, where the salts in an actual experiment are nearly in the same proportions as here taken, as they were generally found to be.

The quantities of nitrite and of gases yielded by the peroxyaminesulphonate may also be each determined directly. The nitrite may be estimated by the urea method, as stated on page 24, most of the sulphonate salts having first been crystallised out and washed with alcohol. The method for collecting and measuring the gases produced during the decomposition consists in letting this proceed in a closed vessel from which the air is withdrawn. A stout-walled,

cylindrical bolt-head, of about 250 c.c. capacity, with a stopcock sealed on to it, was exhausted and then opened with its mouth in the solution of peroxylaminesulphonate and potassium hydroxide. About 200 c.c. were allowed to enter, holding between 6 and 7 grams of the salt in solution. The tube was again exhausted and the stopcock being then closed, the salt was decomposed by heating the solution. When cold, the apparatus was connected with a Sprengel-pump and the gases drawn off and measured. They proved to be free from nitric oxide, but, on treatment with strong alcohol, a small proportion of nitrogen remained undissolved. The experiments with this method of determining the gases have been very few and not such as have admitted of their utilisation in this paper, beyond giving proof that nitrogen in small quantity is generated along with the nitrous oxide, which is the main constituent of the gaseous mixture, and that the quantity of the gases may vary greatly in different experiments.

Where the decomposition of the peroxylaminesulphonate proceeds in the presence of lead peroxide, as it is made to do in the preparation of hydroxylaminetrisulphonate, no hydroxylamine-disulphonate can remain in the solution, and in place of it is found principally an increase in the quantities of trisulphonate and nitrite. The absence of the disulphonate simplifies the analysis as is seen on page 23.

Eight analyses of the products of the spontaneous decomposition of the peroxylaminesulphonate were made. In Expt. 1, a solution holding 2.3184 grams of potassium peroxylaminesulphonate and 60 c.c. of N/10 solution of potassium hydroxide was made up to 150 c.c. and then found to weigh 150.79 grams. It was slowly heated to the boiling point, and kept boiling till decolorised. Expt. 2.—The solution weighing 234.3 grams and containing 2.547 grams of the salt and 72.3 c.c. of N/10 potassium hydroxide was left in the cold

for two days, and then boiled till colourless. During the boiling a reflux condenser was used to retain the water in the solution.

Expt. 3.—A solution weighing 120.42 grams and measuring 120 c.c. of 1.22 grams of salt and 11.4 c.c. of N/10 potassium hydroxide was decomposed by boiling.

Expt. 4.—The solution weighed 134.9 grams and contained 1.8576 grams of salt and 30 c.c. of N/10 potassium hydroxide; it was decomposed by boiling.

Expt. 5.—A solution of 0.6601 grams of salt and 26 c.c. of N/10 potassium hydroxide, weighing 34.25 grams, was left in the cold for a week, when it had become colourless.

Expt. 6.—Like the last, but the solution weighed 266.7 grams and the salt 5.27 grams, whilst the potassium hydroxide was taken in about the same proportion as before.

Expt. 7.—The solution was a portion of the same as had been used for Expt. 2. When kept in a closely stoppered flask, it had only lost all its colour after about five months.

Expt. 8.—This experiment differed from the others in the use of baryta-water in place of potassium hydroxide, and to this must be attributed the production of so much sulphate and hydroxylaminedisulphonate. The solution took a month to lose all its colour.

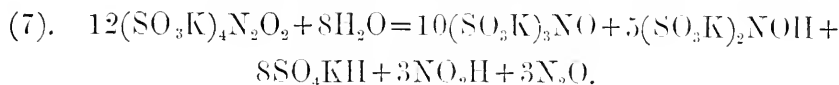
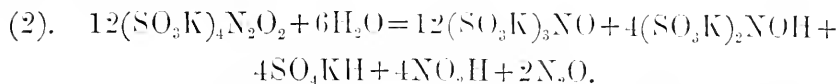
In the table, the numbers of molecules of the several products yielded by  $100(\text{SO}_3\text{K})_4\text{N}_2\text{O}_2$  are given according to calculation from the analyses made in the way above described, and without any corrections for the probable, but variable, errors inherent in the method.

Mol. weight.	1.	2.	3.	4.	5.	6.	7.	8.
$(\text{SO}_3\text{K})_3\text{NO}$ ,	85	102.3	101.7	77.7	91.4	85.3	86	12.9
$(\text{SO}_3\text{K})_2\text{NOH}$ ,	61	30	23.6	65.4	42.3	42	40.4	133.2
$\text{SO}_4\text{KH}$ ,	23	33	47.6	36	41.2	60	61.2	94.7
$\text{HNO}_2$ ,	49	36	32.5	50.2	35	37	26.4	—

Without further experiments, it does not seem possible to account for the wide variations in these numbers, except where baryta was



used. From Expts. 2 and 7, started on portions of the same solution, it seems clear that, with the slow decomposition of the peroxyaminesulphonate which goes on in the cold, instead of the rapid change which occurs at a boiling heat, molecular quantities of hydroxylamine-disulphonate and sulphate take the place of some of the hydroxylaminetrisulphonate, and that a little of the hydroxylamine-disulphonate is replaced by its equivalent of sulphate and nitrous oxide. This becomes more obvious when equations in these two cases are given with only 12 molecules instead of 100 molecules of decomposing peroxyaminesulphonate. This is possible without deviating from the numbers found more than the imperfections of the analytical method allow.



The production of small quantities of nitrogen and aminemono-sulphonate is of necessity ignored in the above calculations.

The author gratefully acknowledges his indebtedness to Dr. Divers. F. R. S., for a thorough revision of his manuscript.





## Peroxyaminesulphonic Acid.

By

**Edward Divers, M. D., D. Sc., F. R. S.**

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Although unrecorded in works on chemistry or chemical technology, it has long been known to inspectors and workers of the lead-chamber process for manufacturing sulphuric acid, that when, through improper working of the chambers, sulphur dioxide is allowed to pass into the Gay-Lussac tower, it produces with the nitrososulphuric acid, also present in the tower, what is called "purple acid," together with an effervescence due to the escape of nitric oxide (Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, **21**, 1492). Sabatier has shown (*Compt. rend.*, 1896, **122**, 1417, 1479, and 1537; **123**, 255) how to give an intensely bluish-violet colour, evidently the same as that of "purple acid," to the monohydrate of sulphuric acid holding nitrososulphuric acid in solution, either by passing sulphur dioxide into it, or by mixing it with sulphuric acid of similar strength containing dissolved sulphur dioxide. Such a sulphuric acid solution of sulphur dioxide may also be treated for some time with a current of nitric oxide and air; or, excluding air, the nitric oxide alone will produce the colour, when a very small quantity of either copper

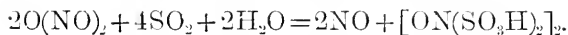
sulphate or ferric or ferrous sulphate has been previously dissolved in the acid. Lastly, certain metals and other substances serve to produce this colour, or a modification of it, by acting on nitrososulphuric acid in monohydrated sulphuric acid, among them being finely divided copper, silver, or mercury. Sabatier has not isolated the substance which gives this violet colour to sulphuric acid treated by the foregoing processes, but has suggested that it may be the unknown acid of Fremy's *sulphazilate*, which he renames *nitrosodisulphonic acid*.

Now, in the preceding paper on peroxyaminesulphonates, Haga has adduced reasons for doubting the correctness of Sabatier's suggestion that the bluish-violet acid is sulphazilic acid, that is, peroxyaminesulphonic acid. There is also one consideration which, although not mentioned by Haga, may nevertheless have affected his judgment. This is the fact that a substance which according to Haga's most conclusive evidence, must be a peroxide, should be produced in the ways prescribed by Sabatier. But this difficulty and those raised by Haga all seem to disappear when the changes which give rise to the acid and the very different conditions for the production of the salt and of the acid are all more closely examined, and leave nothing in the way of accepting the view that this acid is peroxyaminesulphonic acid.

The fact that the violet acid is dissolved in sulphuric acid, whereas the violet salt is in aqueous solution, has to be taken into account when the differences in the behaviour of the two are under consideration. It will then be seen that these differences are really not greater than those between a sulphuric acid solution of nitrous acid (as nitrososulphuric acid) and an aqueous solution of potassium nitrite. The latter when acidified and the former when diluted both quickly lose most of the nitrous acid, there being no stable existence of this acid in the intermediate conditions. Potassium nitrite is

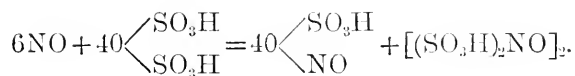
unaffected by hydrogen peroxide or potassium permanganate, being, in fact, producible from nitric oxide by alkaline hydrogen peroxide (Carpenter and Linder, *loc. cit.*), and from hyponitrite by permanganate (Thum, *Monatsh.*, 1893, **14**, 294), whereas nitrous acid is converted by these reagents into nitric acid. Lead peroxide may therefore very well be active towards a sulphuric acid solution of peroxyaminesulphonic acid, although it does not interact with an aqueous solution of its salts. Again, that sulphur dioxide should not interact with peroxyaminesulphonic acid in presence of much sulphuric acid, and yet be very active towards a salt of the acid in water, may well be an instance of what indeed happens in case of mercuric oxy-salts, on which, in presence of much sulphuric acid, sulphur dioxide is no longer active (this Journal **1**, 106), or in that of ferric salts, which are very much more easily reduced by sulphur dioxide in the absence of sulphuric acid than in the presence of excess of it. Similarly, it may further be properly maintained that it does not follow that hydroxylaminetrisulphonic acid should be produced from peroxyaminesulphonic acid in sulphuric acid solution because its salt is produced in a neutral or an alkaline aqueous solution of a peroxyaminesulphonate. This contention being admitted, the non-formation of this acid, observed by Haga, is not significant.

Since the well-known compound, nitrososulphuric acid, is not a sulphonic derivative, as Sabatier takes it to be, but the mixed anhydride of nitrous and sulphuric acids, the nature of its conversion into the violet acid is easy to understand. Regarding the mixed anhydride as being simply nitrous anhydride (the sulphuric acid being undecomposed), the production from it of nitric oxide and peroxyaminesulphonic acid is seen to be only its usual decomposition into nitric oxide and nitric peroxide, except that the latter product is now sulphonated:

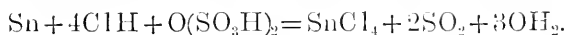


When metallic copper is used in place of sulphur dioxide, the generation of the necessary sulphur dioxide by the action of the metal on the pyrosulphuric acid or the nitrososulphuric acid, only introduces an interesting complication. Pyrosulphuric acid at once interacts with copper in the cold (*J. Chem. Soc.*, 1885, **47**, 638).

There remains to be considered the production of the "purple acid" along with nitrososulphuric acid from nitric oxide and sulphuric acid in the presence of cupric or ferric sulphate as a catalytic agent. The sulphuric acid being represented as existing in its pyro-state (the form in which it acts in presence of an oxide of nitrogen), the change is expressed by the equation



As to the peroxidising action of sulphuric acid here shown, it may be well to recall the action of the acid upon metallic tin in presence of hydrochloric acid (Henmann and Koechlin, *Ber.*, 1882, **15**, 420):



In this equation the stannic chloride and the sulphur dioxide together take the place of the peroxyaminesulphonic acid in the previous one, for  $[\text{ON}(\text{SO}_3\text{H})_2]_2$  can evidently be expanded into  $\text{N}_2\text{O}_4 + 4\text{SO}_2 + 2\text{OH}_2$ .

It is difficult to conceive of any other rational interpretations of Sabatier's remarkable results than those given above, and these are all consistent with the assumption that the purple acid is not merely isomeric, but actually identical with peroxyaminesulphonic acid, and is therefore a peroximide and an exclusively tervalent nitrogen compound.



## Constitution of Nitric Peroxide.

By

Edward Divers, *M. D., D. Sc., F. R. S.,*

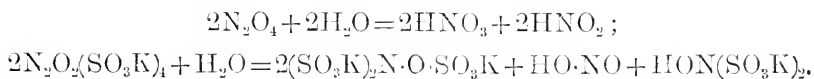
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In a paper appearing with this (this vol., Art. 15), Haga has demonstrated that Fremy's *sulphazilate* is an oxime-peroxide and a tervalent nitrogen compound. If Hantzsch and Semple's suggestion is accepted (*Ber.*, 1895, **28**, 2744; *cf.* Piloty and Schwerin, *Ber.*, 1901, **34**, 1884 and 2354), that Fremy's salt is also a sulphonated nitric peroxide, it follows that the constitution of nitric peroxide is at last determined, being that of *nitrosyl peroxide*. Hantzsch and Semple must be right, for, after Haga's researches, a sulphazilate as a peroxy-aminesulphonate cannot be supposed to be other than a sulphonated nitric peroxide. It only remains, therefore, to show that nitric peroxide is a true peroxide in its chemical relations.

It is formed from nitric oxide and oxygen, just as sodium peroxide is formed from sodium and oxygen. Nitrous acid cannot, indeed, be shown to pass simply into it and back again, as a hydroxylaminedisulphonate (sulphonated nitrous acid) changes into a peroxyaminesulphonate, but that is only on account of its own instability and that of nitrous acid.

Its interaction with organic oximes, in which it converts these substances into peroxides and becomes hydrogenised into nitrous acid (Scholl), is in accordance with its nature as a true peroxide. Similarly, it converts a hydroxylaminedisulphonate into a peroxyamine-sulphonate (Haga).

Nitrosyl peroxide and a peroxyaminesulphonate both interact with water in essentially the same way, the apparent difference being due to the limits imposed by the sulphonation in the case of the latter substance. The former yields half its nitrogen as nitric acid and half as nitrous acid, whilst the latter yields half its nitrogen as a mixed anhydrosulphate (hydroxylaminetrisulphonate) and the other half as nitrous acid and sulphonated nitrous acid (hydroxylaminedisulphonate):



It would seem, therefore, that wholly on the evidence afforded by Haga's work, it can now be confidently asserted that dinitric peroxide is nitrosyl peroxide and a compound of exclusively tervalent nitrogen. The constitution of mononitric peroxide, in regard to these two points, remains to be considered, but can hardly be very different.

Hantzsch and Semple have suggested (*loc. cit.*) that the bluish-violet dissolved form of a peroxyaminesulphonate corresponds with mononitric peroxide, and its crystalline form with dinitric peroxide. Since then, Piloty and Schwerin (*loc. cit.*) have expressed the belief that *porphyrexide*, which has the colour of mononitric peroxide, may also be a derivative of this peroxide, because it contains the group :NO singly, as shown by the formula  $(\text{C}_5\text{H}_9\text{N}_3) : \text{NO}$ . Its molecular weight, however, has been only indirectly ascertained, that is, by cryoscopic determinations of those of its nitrate and its chloro-derivatives. That its molecular weight is not double as great is a remarkable fact, for, in its chemical behaviour, and especially in its



reversible relation with *porphyrexine*,  $(C_5H_9N_3):NOH$ , porphyrexide seems to belong to the class of oxime-peroxides. Piloty and Schwerin do not indeed recognise this, and have instead come to the conclusion that the nitrogen of the group  $:NO$  in porphyrexide and in mononitric peroxide must be quadrivalent. In the light of Haga's experimental results, this view of the matter has become untenable, since porphyrexide and the peroxyaminesulphonates appear to belong to the same class of nitroso-compounds, as Piloty and Schwerin themselves have pointed out.

In the few cases in which it has been possible to determine cryoscopically the molecular weight of a glyoxime-peroxide, this has been found to include  $:NO$  twice. This result may be owing to the glyoxime constitution of these peroxides, but even so there is still no peroxide, except mononitric peroxide, and possibly porphyrexide, the molecular weight of which is such that it contains the group  $:NO$  only once. The occurrence of many nitroso-compounds in a colourless, solid form, and in a bluish-violet liquid form, does not lend much assistance in deciding the molecular weights of the two forms of a peroxyaminesulphonate, since they contain not  $:NO$  but  $\cdot NO$ . But it must not be left out of sight that Piloty (who thinks otherwise, and has been followed by Schmidt, Bamberger and others) has succeeded in showing that the white form of these compounds contains the group  $\cdot NO$  twice, and that the deeply-coloured modification contains it only once. But here the latter is the form which must be treated as the chemically active one, whilst the double weight found for the white form has to be left uninterpreted chemically, as, for example, in the case of the formula  $(C_8H_{17}NO)_2$  for nitroso-octane.

In the paper by Hantzsch and Semple (*loc. cit.*) there occurs, but in a foot-note only and without comment or explanation, the punctuated formula  $O:N:(SO_3K)_2$ ; whether this is to be regarded as a

printer's error for  $O:N:(SO_3K)_2$  is uncertain, but if it is not it indicates some recognition by these chemists of the presence of univalent oxygen. However this may be, the possibility of the nitrogen being quadrivalent being inadmissible, the only solution of the matter seems to be to consider that both mononitric peroxide and porphyrexide are compounds of univalent oxygen, although still peroxides. The fact that a molecular quantity, such as that formulated by  $HO$ ,  $NO_2$ ,  $(SO_3K)_2NO$ , or  $(C_5H_9N_3)NO$ , is never met with singly in chemical interactions militates against the acceptance of this explanation. Piloty and Schwerin, in discussing the quadrivalency of nitrogen, conceal this fact by stating that porphyrexide is produced from porphyrexine by the action of *half an atom* of oxygen. It is much more correct to hold with Haga that the molecule of peroxyaminesulphonate, and therefore also of mononitric peroxide and of porphyrexide, is not less than that represented by  $[NO(SO_3K)_2]_2$ ,  $(NO_2)_2$ , or  $(C_5H_9N_4O)_2$ , as the case may be, if by molecule is meant the smallest chemically active weight of a substance. But still the fact remains that, when measured by comparison of their physical properties, the molecular weights of porphyrexide and red nitric peroxide are expressed by half the above formulae, and probably the bluish-violet form of a peroxyaminesulphonate has also a molecular weight, which when physically considered, should be expressed by the formula,  $NO(SO_3K)_2$ . These weights, only physically determined, have no chemical significance, and should be distinguished from their doubles, the truly chemical molecular weights. But, as pseudo-chemical molecules, they must be represented to contain a univalent atom of oxygen.

It is, after all, not so difficult to admit that oxygen may be univalent in a peroxide. In fact, true peroxide may be defined and differentiated from other oxides, as being a compound in which some or

all of the oxygen is exerting on the rest of the compound only half its usual valency. Or, conversely, a peroxide may be defined as a compound containing oxygen which is either actually univalent or exteriorly and quasi-univalent. Apart from the unfamiliar nature of the conception of actually univalent oxygen, it seems natural enough to find a normal molecule of nitric peroxide dissociate at a gentle heat into two identical but simpler ones, in consequence of the linked oxygen atoms becoming parted and losing valency. On the other hand, the assumption that nitrogen is quardrivalent does not accord with the result actually obtained, when by cooling nitric peroxide it is found that the valency of the nitrogen decreases instead of increasing,  $2\text{O}:\text{N}:\text{O}$  becoming  $\text{O}:\text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N}:\text{O}$ .





## Ueber das Vorkommen von *Saccharomyces* *anomalus* beim Sakebrauen.

VON

K. Saito, *Rigakushi.*

Am Beginn des Jahres 1903 hatte ich Gelegenheit, einige Proben von frischem Sake aus verschiedenen Ortschaften<sup>1)</sup> Japans zu erhalten; alle erlitten allmählich die überall vorkommende bakterielle Trübung, und dann bildete sich auf der Oberfläche der Flüssigkeit eine weissgraue, feinfaltige Kahlhaut. Von der letzteren wurde eine Art der Kahlhefe, die leicht endogene Sporen bildet, isoliert. Das Vorkommen derartiger Pilze bei der Sakebrauerei ist schon in den Untersuchungen KLÖCKER und SCHÖNNING's<sup>2)</sup> erwähnt. YABE<sup>3)</sup> hatte auch eine *Mycoderma* im Reisstroh der Sakebrauereien konstatiert. Nach KOZAI<sup>4)</sup> kommen im Koji zwei Arten der Kahlhefen stets vor, darunter eine Form mit endogenen, hutförmigen Sporen. Mit welcher der in den Arbeiten erwähnten Formen unsere Art identisch ist, sind wir nicht im Stande festzustellen, weil in den Arbeiten keine einschlägigen Versuche über

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1) Nada, Itami und Ikeda (Provinz Settsu), Sakai (Prov. Idsumi), Muroyama (Prov. Ise), Handa und Kanesaki (Prov. Owari).

2) KLÖCKER, A. und SCHÖNNING, H.: *Centralbl. f. Bakt., Abth. II*, Bd. I, 1895, p. 777.

3) YABE, K.: *Bulletin imperial University Tokio, College of Agriculture*, Vol. III., 1897, No. 3, p. 221.

4) KOZAI, Y.: *Chemische und biologische Untersuchungen über Sake-Bereitung*, *Centralbl. f. Bakt., Abth. II*, Bd. VI, 1900, p. 385.

die Formenmannigfaltigkeit und Lebensgeschichte der Kahlmhefe angestellt sind. Doch halte ich eine Gleichheit mit einem der Pilze für das Wahrscheinliche, weil unser Pilz sowohl in Koji, Maisch und Sake gefunden wurde.

Meiner Ansicht nach darf die Verfolgung der Formenmannigfaltigkeit und Lebensgeschichte, besonders der Stoffwechselprodukte eines solchen Organismus ein hohes Interesse beanspruchen, da die Umsetzungen, welche er in den gährfähigen oder vergohrenen Flüssigkeiten hervorzurufen im Stande ist, ein grosses Gewicht im Gährungsgewerbe haben. Sogar dann, wenn derartige Beziehungen heutzutage noch unvollkommen erkannt sind, darf man solche Studien nicht ganz ausser Acht lassen, da sie uns mit dem Verhalten der Kahlmhefe bei einem bisher in dieser Hinsicht kaum studierten Gewerbe bekannt machen und zugleich unsere Kenntniss über die Kahlmhefe an sich mehr oder weniger erweitern.

## I. MORPHOLOGIE.

1. *Formen der Kolonien auf den Platten.* Die Kolonienbildung unseres Sprosspilzes wurde auf Würze- und Kojidekoktagelatineplatten genauer verfolgt. Die Formen der Kolonien waren nie beständig, auf denselben Platten aber stets konstant.

Die oberflächlichen Kolonien erschienen als kleine, runde, weisse Punkte; im älteren Stadium der Entwicklung wurden sie etwas gebuchtet, wenig erhaben, trocken mehlig, porzellanweiss und undurchsichtig, radial und konzentrisch fein gefaltet. Der Rand ist unregelmässig gewulstet, nie aber baumartig verästelt (Fig. 1). Auf Kojidekoktagarplatten zeigten sich nur selten flach ausgebreitete, glatte, unregelmässig gestaltete Kolonien. Die untergetauchten



Fig. 1. Oberflächliche Kolonie.

Kolonien waren in den jugendlichen Stadien durchwegs kreisrund oder ellipsoidisch-oval, glatt und undurchsichtig; auch bei weiterer Entwicklung behielten sie ihre Formen.

2. *Riesenkolonien.* Die Riesenkolonien wurden auf Würzegeatine bei Zimmertemperatur herangezogen. Das Wachstum war sehr träge. Die Kolonie ist längsriefig und gekerbt. Im Zentrum ist sie etwas erhaben und zeigt dort eine gelbliche Farbe. In einiger Entfernung ziehen sich um das erhabene Zentrum konzentrische Ringe, die durch die nun zum Rande verlaufenden Längsriefen in zahlreiche Theilchen zerlegt werden (Fig. 2).

3. *Stichkulturen.* In Würzegeatine gestochen, wuchs der Kopf trockenmehlig und zeigte ein gleiches Aussehen wie eine Zwergkolonie. Die Stichlinie bekam selten ein körniges Aussehen.



Fig. 2. Riesenkolonie.

4. *Strichkulturen.* Der Strich auf Würzegeatine wuchs in Zimmertemperatur schon nach einem Tage. Er ist meist mehlig-trocken, dick und breit mit fein gestreiftem, selten glatt saftigem Rande versehen. Sowohl in Strich- als in Stichkulturen begann die Verflüssigung der Gelatine bereits nach zwei Wochen (Fig. 3).

5. *Kahmhautbildung.* Wenn unser Pilz in Würze, Kojidekott oder irgend einer zuckerhaltigen Nährflüssigkeit bei 28°C kultiviert wurde, trat die Kahmhaut schon nach 24 Stunden auf. Die Haut ist grauweiss, trocken und wird später gefaltet; sie



Fig. 3. Strichkultur auf der Gelatine.

besteht aus lebhaft sprossenden Hefezellen, zwischen welchen eingemischt reichliche Gasblasen vorkommen.

Mit der Gährung schreitet die Haut in der Entwicklung immer fort und zieht sich als Ring über das Flüssigkeitsniveau an der Glaswand empor; sie bleibt nach Neigen des Gefässes an derselben haften.

Sobald die Gährung vollendet ist, sinken die angefeuchteten Zellen allmählich zu Boden. Die Bodenmasse erscheint anfangs grauweiss, später aber etwas bräunlich; die Zellen werden dickwandig und vakuolenhaltig. Gleichzeitig mit der Bildung des Bodensatzes entsteht auf der Oberfläche eine sekundäre Haut, welche dünn und durchsichtig, fettglänzend und fein gestreift ist.

6. *Kultur in Gelatinetropfen.* In einem Tropfen 10 % Würzegeatine bildet der Pilz eine weisse kleine Kolonie, die unter schwacher Vergrösserung kreisrund und stets glattrandig erscheint. Nach einiger Zeit beginnt die Gelatine um die Kolonie herum allmählich verflüssigt zu werden.

7. *Zellformen,-grösse und-inhalt.* Die Formen der Zellen sind rundlich bis eiförmig, treten sowohl als Einzelglieder, wie bisweilen auch zu kleinen Sprossverbänden vereinigt auf. Die Formen bieten nach der Art der Nährsubstrate kleine Schwankungen. Doch sind die Grössenschwankungen nicht von Bedeutung. Im Durchschnitt wurden gemessen: a) längliche Zellen  $10-20\ \mu$ :  $3-4\ \mu$ ; b) rundliche eiförmige Zellen  $6-8\ \mu$ :  $2-4\ \mu$ .

Die jugendlichen Zellen sind klar, plasmareich, kleine, stark lichtbrechende Körnchen führend, bisweilen auch vakuolig. Bald



früher, bald später wird der Inhalt jedoch gekörnt und die Wand stark verdickt, wobei sich seltener die Zelle unregelmässig gestaltet (Fig. 4).

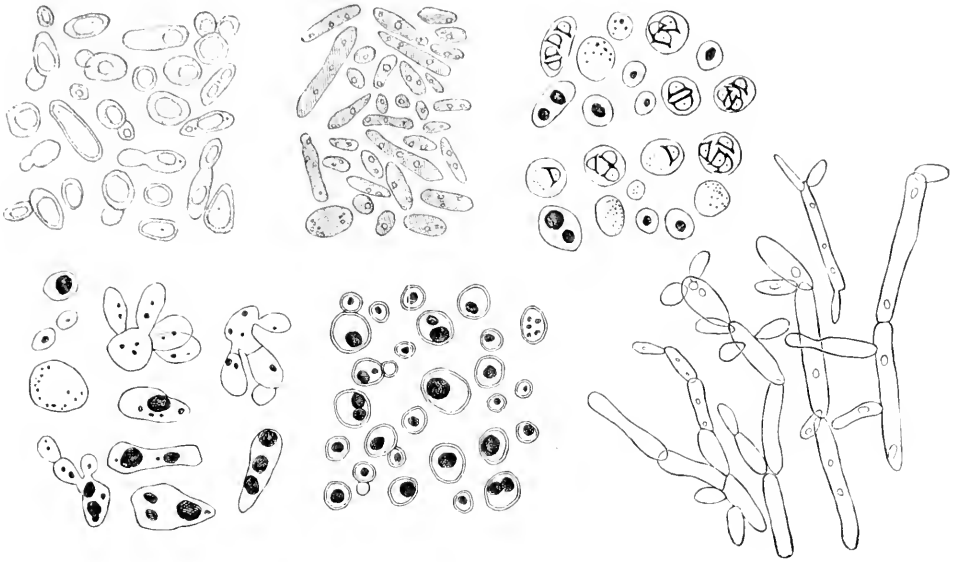


Fig. 4.: Verschiedene Formen der Zellen ( $\times 900$ ).

8. *Sporenbildung.* Die Sporen konnten bei unserem Pilze leicht auf verschiedenen Substraten, sowohl auf festen (Gelatine, Agar oder Gipsblöcken) als auch auf flüssigen, beobachtet werden. Die Sporen sind hutförmig und 2–4 in einer Zelle eingeschlossen.

## II. PHYSIOLOGIE.

### 1. VERHALTEN GEGEN KOHLENHYDRATE.

Um das Verhalten unseres Sprosspilzes gegen verschiedene Kohlenhydrate näher zu bestimmen, unternahm ich eine Reihe

von Versuchen mit Dextrose, Laevulose, Saccharose, Maltose, Galaktose, Dextrin, Inulin und Stärkekleister. Für die Kultur diente mir die MAYER'sche Lösung mit 15 % Kohlenhydrat. Sie bestand aus :—

15.0 Gramm	Kohlenhydrat.
1.0 „	Weinsaures Ammon.
0.5 „	Kaliumphosphat.
0.25 „	Magnesiumsulfat.
0.05 „	Calciumphosphat.
100.0 c.cm.	Destilliertes Wasser.

Gleichzeitig unternahm ich, die Wirkung der Hefe auf der Würze und dem Kojidekokt zu ermitteln.

Nach Impfung mit Platin-öse standen die Kulturgläser in 28°C. In Dextrose, Laevulose, Saccharose, Galaktose trat die Gasentbindung schon nach 24 Stunden deutlich auf, dagegen in Maltose nur spärlich. Obschon die Entwicklung der Hefe in Inulin und Dextrin ziemlich gut vor sich geht, findet dabei doch keine Gasentbindung statt, und in Stärkekleister kommt fast keine Entwicklung zu Stande. Bezüglich der Gährverhältnisse verhalten sich Kojidekokt und Würze gerade umgekehrt, weil die Gasentbindung im ersteren sehr stark, aber im letzteren nur spärlich eintritt. Der Grund dieser Erscheinung liegt vielleicht an dem Reichtum der Maltose in der Würze und der Dextrose im Kojidekokt.

Die Hauptgährung in Dextrose, Laevulose und Galaktose dauerte 2½–3 Wochen lang; sie war kürzer in Maltose und Saccharose. Schnell endete die spärliche Gasentbindung in der Würze, die dann etwas lichtgelb entfärbt wurde.

## 2. GÄHRPRODUKT.

a) Gas. Im Gährungsrohre mit Dextrose-MAYER'scher Lösung entwickelte sich eine Menge Gas, welches von Kalilauge fast gänzlich absorbiert wurde. Daraus erkennen wir, dass bei der Gährung eine reichliche Menge Kohlensäure entstanden war. Der übrige Theil des Gases war so klein, dass keine weiteren Versuche möglich waren. Doch hielt ich den Ueberrest für die Luft, welche sich mit den Hefenzellen in der Flüssigkeit eingemengt vorgefunden hatte.

b) Alkohol. Das Destillat aus 16-tägiger Kulturflüssigkeit mit Dextrose roch stark geistig und enthielt eine mittelst der Jodoformreaktion nachweisbare Alkoholmenge. Nach Berechnung des mit Hilfe der GAY-LUSSAC'schen Alkoholmeter bestimmten Alkoholgehaltes an originalen Volumen der Kulturflüssigkeit ergaben sich ca. 5 %. Höhere Alkohole wie Propyl-, Butyl- und Amylalkohol konnte ich nicht feststellen.

c) Säure. Um die Art der gebildeten Säuren zu bestimmen, sind die Kulturen in Dextrose-MAYER'schen Lösungen am meisten zu empfehlen, weil hierbei die Gährungserscheinungen sehr stark zu Tage treten.

Von einer 16-tägigen Gährflüssigkeit—500 c. cm—wurden zunächst die event. entstandenen flüchtigen Säuren destilliert, bis das emporsteigende Destillat nicht mehr sauer reagierte. Das Destillat enthielt an Säure insgesamt entsprechend 106.75 c. cm  $\frac{1}{10}$  NaOH, d. i. auf Essigsäure berechnet insgesamt : 0.6405 g flüchtige Säure. Diese Menge an flüchtiger Säure ist also bei der Gährung in 500 c. cm Kulturflüssigkeit gebildet worden. Infolgedessen beträgt der Gehalt der vergohrenen Flüssigkeit an flüchtiger Säure pro 100 c. cm : 0.1281 g oder 1.281 %.

Im Destillationsrückstand war an nichtflüchtigen Säuren insgesamt enthalten eine Menge entsprechend  $68.25 \frac{1}{10}$  NaOH, d. i. auf Weinsäure berechnet insgesamt 0.5113 g nichtflüchtige Säure. Infolgedessen beträgt der Gehalt der Kulturflüssigkeit an nichtflüchtiger Säure pro 100 c. cm : 0.1024 g oder 1.024 %.

Zur näheren Bestimmung der einzelnen flüchtigen Säuren wurde alsdann das Destillat mit Soda sorgfältig neutralisiert, und in der neutralisierten Lösung konnte Essigsäure durch die bekannte Eisenoxydsalzreaktion (die dunkelrothe Färbung mit Eisenchloridlösung und das Gelbwerden der dunkelrothen Lösung mit Salzsäure) nachgewiesen werden. Essigsäure in dem Produkte verrieth sich noch weiterhin durch die Bildung des angenehmen, erfrischenden Geruchs—des charakteristischen Geruchs des Essigsäureethylesters—, wenn man die wässrige Lösung der neutralen Natriumsalze mit Alkohol und konz. Schwefelsäure versetzte und gelinde erwärmt. Das Destillat ergab mit ammoniakalischer Silbernitratlösung die Spiegelbildung, doch ging diese Eigenschaft durch langes Aufbewahren des Destillats stets verloren. Auch das Fehlen der Quecksilberoxydreduktion und ameisensaurer Aethylesterbildung lässt den reduzierenden Körper nicht als Ameisensäure annehmen, sondern als ein Aldehyd, welches als ein Zwischenprodukt von Alkohol zu Säure entstanden ist.

Die Entstehung von Buttersäure ergab sich aus dem Auftreten des aromatischen Prinzips der Ananasfrucht, welches bei der Gährung deutlich erkennbar war.

Nachdem die Gährflüssigkeit so lange der Destillation unterworfen worden war, bis das emporsteigende Destillat keinerlei Säurereaktion mehr anzeigte, wurde der eingekochte Destillationsrückstand, welcher stark sauer reagierte, mit Tierkohle entfärbt

und filtriert. Darnach wurde die Lösung der näheren Bestimmung der einzelnen Säuren unterworfen.

Nach Neutralisation mit Ammoniak wurde der Flüssigkeit eine Menge Calciumchlorid beigesetzt und etwa eine Stunde stehen gelassen. Der erhaltene Niederschlag wurde abfiltriert, ausgewaschen und nach Zusatz von kalter Natronlauge wieder filtriert. Der Niederschlag enthielt kein Calciumoxalat.

Dem Filtrate von dem bei  $\text{CaCl}_2$ -Zusatz abgeschiedenen Niederschlage wurde alsdann ein ca. dreimaliges Volumen Alkohol versetzt: es schied sich nunmehr ein weisser flockiger Niederschlag aus, welcher nach Waschen mit Alkohol in Salzsäure gelöst und nach Zusatz von Ammoniak abgekocht und wieder filtriert wurde. In dem so erhaltenen Niederschlage fehlt die Zitronensäurereaktion, aber das Filtrat ergab deutliche Bernsteinsäurereaktion.

Nach dem eben Gesagten konnten an flüchtigen Säuren mit Sicherheit Essigsäure und Buttersäure und an nichtflüchtigen Säuren Bernsteinsäure unter den Gährprodukten erkannt werden. Es ist jedoch keineswegs ausgeschlossen, dass auch noch Spuren anderer Säurearten bei der Gährung entstanden sind.

d) Ester. Mit der Bildung dieser Säuren neben der Alkoholproduktion hing zweifellos das Auftreten des aromatischen Prinzips zusammen, das den Kulturen einen angenehmen Geruch verlieh. Dasselbe ist hauptsächlich ein Gemenge des essigsauren und buttersauren Aethylesters.

### 3. TEMPERATUREINFLUSS.

Nach dem Angensehein des Wachstums auf der Strichfläche liegt die optimale Temperatur des Pilzes bei  $28^\circ\text{C}$ . Er ist jedoch

im Stande, bei 15°–37°C wohl zu wachsen und die Kahlhaut zu bilden. Bei 10°C wird das Wachsthum sehr träge.

Um die Widerstandsfähigkeit unserer *anomalus*-Art gegen Erhitzen zu prüfen, wurden die Reagensgläser, die mit 10 c. cm. Kojidekokt beschickt waren, mit einer geringen Menge der eintägigen Kulturen geimpft, 5 Minuten lang bei 50°, 55°, 60°, 65°, 70°, 75°, 80° und 85°C erwärmt, und dann schnell abgekühlt. Nach einem Tage hatten eine volle Decke auf dem Kojidekokt gebildet die Kulturen, die bei 50°, 55° und 60°C erwärmt wurden. In den übrigen Gläsern war es zu keiner Entwicklung gekommen.

### III. ALLGEMEINES.

Nachdem HANSEN<sup>1)</sup> die Abhandlung über *Saccharomyces anomalus* veröffentlicht hatte, wurde der Organismus und seine Eigenschaften von einigen Autoren näher studiert. FISCHER und BREBECK<sup>2)</sup> unterscheiden von *S. anomalus* die sogenannte *Endoblastoderma pulverulentum* durch die beim letzteren vorkommende endogene Zellbildung. Mit den Vermuthungen KLÖCKER's<sup>3)</sup> verliert jedoch die Annahme FISCHER und BREBECK's den Boden, und die *Endoblastoderma pulverulentum* genannte Form ist nichts anderes als echter *S. anomalus*.

STEUER<sup>4)</sup> hatte vier verschiedene Rassen derartiger Or-

1) HANSEN, E. CHR.: Sur la germination des spores chez les Saccharomycetes. Comptes-rendus des travaux du laborat. de Carlsberg, Vol. III, livr. 1, Kopenhagen 1891.

2) FISCHER, B. und BREBECK, C.: Zur Morphologie, Biologie und Systematik der Kahlpilze, der *Monilia candida* Hansen und des Soorerregers, 1894.

3) KLÖCKER, A.: Untersögelser over Saccharomyces Marxianus, *S. apiculatus* og *S. anomalus*. (Ref. in Bot. Jahresbericht, 1895, Bd. I, p. 169).

4) STEUER, L.: Zeitschrift für das ges. Brauwesen, 1900, No. 1–3. (Ref. in Centralbl. f. Bakt., Abth. II, Bd. VI, p. 217).

ganismen untersucht. LINDNER fügt in seinem Werke „Mikroskopische Betriebskontrolle“<sup>1)</sup> noch einige andere Formen der *anomalus*-Gruppe hinzu. In den neueren Arbeiten MEISSNER's<sup>2)</sup> an zahlreichen Kalmhefen findet man drei *anomalus*-Arten.

Mit Rücksicht auf die erwähnten Arbeiten ist es kaum zweifelhaft, dass der im allgemeinen unter dem Namen „*Saccharomyces anomalus*“ gefasste Organismus in einige Varietäten oder Rassen eingetheilt werden muss. Es ist also nicht unnöthig zu diskutieren, welcher der beschriebenen Formen unsere Art nahe steht. Wenn man die von mir selbst zugegebenen Thatsachen berücksichtigt, so bedarf es kaum einer besonderen Erörterung, dass es sich um eine echte *anomalus*-Art handelt. Was ihre morphologischen Eigenschaften betrifft, steht sie mit dem MEISSNER'schen *S. anomalus* No. 7 in nächster Verwandtschaft.

In physiologischer Hinsicht sind am ersten die Gährverhältnisse zu betrachten. STEUBER's *anomalus*-Art No. 1 kann Saccharose, Dextrose und Lävulose vollständig vergähren, und zwar unter Bildung von Alkohol, Essigsäure und Essigäther, während No. 2, 3 und 4 nicht im Stande sind, Dextrose, Laktose, Galaktose und Maltose zu vergähren. Auch rufen sie in Lävuloselösungen nur schwache Alkoholbildung hervor. Durch die MEISSNER'schen drei *anomalus*-Arten waren reichliche Mengen Alkohol gebildet worden, und die analytischen Bestimmungen ergaben bei No. 4 6.01 Vol.-%, bei No. 7 5.03 Vol.-% und bei No. 40 auch 5.03 Vol.-% Alkohol. Ca. 5% Alkoholgehalt betrug die Gährflüssigkeit mit dem BARKER'schen *S. anomalus* (Hansen),<sup>3)</sup>

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1) Dritte Auflage, 1902, p. 381.

2) MEISSNER, R.: Zur Morphologie und Physiologie der Kalmhefen und der kalmhautbildenden Saccharomyceten. Landw. Jahrb., Bd. XXX, 1901, p. 497.

3) BARKER, B. T. B.: A Fragrant 'Mycoderma' yeast, *Saccharomyces anomalus* (Hansen). Annals of Botany, Vol. XIV, 1900, p. 215.

welcher Dextrose, Laevulose und Saccharose lebhaft vergähren konnte.

Die von mir untersuchte *anomalus*-Art ähnelt demnach dem *S. anomalus* No. 1 STEUBER's, No. 7 und No. 40 MEISSNER's und auch der von BARKER untersuchten *anomalus*-Art.

Besonders erwähnenswert ist auch die Widerstandsfähigkeit der *anomalus*-Art gegen Erhitzen. BARKER's *anomalus*-Art wurde durch 5 Minuten langes Erhitzen bei 55°C getötet. Jüngere Zellen der MEISSNER'schen *anomalus*-Arten, die 2 Stunden lang bei 45°C im Moste erwärmt wurden, haben nach 2 Tagen auf der Oberfläche des Mostes eine volle Decke gebildet. Unsere Art widerstand dem 5 Minuten langen Erhitzen bei 60°C, erst durch gleichdauerndes Anwärmen bei 65°C aber starb sie gänzlich ab.

Ausser der spezifischen Verschiedenheit der Widerstandsfähigkeit der Zellen beruhen die verschiedenen Resultate theils auf dem Alter der geimpften Hefezellen,<sup>1)</sup> theils auf der chemischen Zusammensetzung der hierbei angewandten Flüssigkeit.

Was die gelatineverflüssigende Fähigkeit der *anomalus*-Art betrifft, so haben wir auch hier einige verschiedene Angaben. WEHMER<sup>2)</sup> fand, dass *S. anomalus* die Gelatine nicht verflüssigt, und gleichzeitig bemerkte er, dass die von FISCHER und BREBECK beschriebene *Endoblastoderma pulverulentum* den Boden peptonisieren könne. Aber wir sind, nach meiner Ansicht, nicht im Stande, mit diesem Unterschiede allein beide Formen als verschiedene Arten von einander zu trennen, da die Untersuchungen BARKER's lehren, dass *S. anomalus* nach gewissen Kulturbedingungen auf der Gelatine mannigfache Wirkungen ausübt,

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1) MEISSNER (l. c.) hatte den Nachweis geliefert, dass die Widerstandsfähigkeit der Kalmhefe gegen die Erwärmung mit zunehmendem Alter zunimmt.

2) WEHMER, C.: Ueber die Verflüssigung der Gelatine durch Pilze. Chemiker-Ztg., 1895, No. 9, 2088.



so in einem Falle sie schnell verflüssigend, im anderen Falle aber sehr langsam. Unsere *anomalus*-Art verflüssigt auf der Strichfläche die Gelatine stets langsam, und es scheint mir wahrscheinlich, dass die Thätigkeit im höchsten Masse von der Temperatur abhängig ist.

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Ueber die Rolle, welche *S. anomalus* im Sakebereitungsprozesse spielt, liegt noch keine Ansicht vor. Es taucht mir die Vermuthung auf, dass das bei der Reifung der Sakemaische bemerkbare angenehme Esteraroma der Hauptsache nach der Masse des stets vorkommenden *S. anomalus* zuzuschreiben sei. Es lässt sich nun fragen, wie diese Hefeart mit der eigenen Sakehefe während des Gährverlaufes in Konkurrenz tritt, und wann die Arbeit der einen endet und die der anderen beginnt. Die Beantwortung dieser und anderer hieran anzuknüpfender Fragen behalte ich mir für die Zukunft vor. Es sei hier hinzugefügt, dass die Widerstandsfähigkeit unserer *anomalus*-Art gegen Alkohol sehr niedrig ist; in Saccharose-MAYER'scher Lösung mit 10% Alkohol kann diese Art nicht zur Entwicklung kommen, während sie 5% Alkoholgehalt zu ertragen im Stande ist.

Nach einer mündlichen Mittheilung von Herrn Professor Dr. MIYOSHI beobachtet dieser sehr oft spontane Alkoholgährung des Blutungssaftes gewisser Pflanzen, hervorgerufen durch *S. anomalus*. In einer noch nicht publizierten Arbeit konstatiert er einen solchen Fall in dem Saft, welcher aus dem gleich über dem Boden geschnittenen Stamm von *Phyllostachys nigra* geflossen war. Aus der Gährmasse isolierte er *S. anomalus*, welcher die Zuckerlösung mit der charakteristischen Esterbildung in Alkohol vergährte. Eine Anzahl anderer Bakterien und Pilze liess sich

auch aus der Masse isolieren, darunter eine sehr auffallende, Buttersäure bildende Bakterienart.

Am Schlusse spreche ich Herrn Prof. Dr. MIYOSHI, unter dessen Leitung meine mykologischen Untersuchungen vor sich gehen, meinen herzlichen Dank aus.

Oktober, 1903.

Botanisches Institut,

Kais. Universität zu Tokio.



**Tieghemella japonica** SP. NOV.

VON

**K. Saito**, *Rigakushi*.

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*Mit 1 Tafel.*

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Im Februar 1903, während meines Aufenthalts in der Stadt Handa, Provinz Owari, unternahm ich eine Untersuchung über die Luftkeime in einem Gährkeller der Sakebrauerei daselbst. Ausser den überall vorkommenden Schimmelpilzen wie *Penicillium glaucum*, *Cladosporium herbarum* u. s. w. fand ich eine interessante Art, welche mit *Tieghemella Orchidis*<sup>1)</sup> viel Aehnlichkeit besitzt, aber wegen ihrer anderen Merkmale als eine Species nova gelten kann. Ich nenne sie somit *Tieghemella japonica*.

**I. MORPHOLOGISCHES.**

Das erste Stadium der Entwicklung des Pilzes auf irgend einem guten Nährsubstrate beginnt mit einem sterilen, schwach verästelten, sich flach ausbreitenden Mycelium, aus welchem das

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1) VUILLEMIN, P., Le genre *Tieghemella*. Bulletin de la Soc. Myc. de France, Tome XIX, 2<sup>e</sup> Fascicule, P. 117.

Luftmycelium schliesslich emporwächst. Das Letztere verzweigt sich, indem es auf der Unterlage in allen Richtungen herumkriecht; dann geht es endlich in Stolonen über.

Die Ausläufer producieren, nachdem sie sich verzweigt und ihr Längswachsthum beendet haben, auf der Unterlage feine, weniger verzweigte Schläuche—Rhizoiden (Fig. 3 und 4). An den verschiedenen Punkten der Ausläufer bilden sich solitäre oder quirlig (2–5) angeordnete Sporangienträger, welche sich wieder verzweigen können. In letztem Falle schliesst jeder Zweig mit einem Sporangium ab. Die Höhe des üppig gewachsenen Rasens ist 1–2 cm.

Am Anfange der Kultur sieht man im ganzen Mycelium nirgends Querwände. In älteren Stadien treten jedoch auf manchen Punkten der Substratmycelien Scheidewände hervor, welche allmählich die Gemmen (Chlamydosporen) abschliessen, wenn auch in Luftmycelien niemals solche Umbildungen vor sich gehen. Stets fehlen die Querwände auf den Rhizoiden.

Die breiten Ausläufer treten vom Substratmycelium (Fig. 7 und 8) empor, und krümmen sich, wenn sie die Höhe von einigen Centimetern erreicht haben, herab, um in Berührung mit dem Substrate die Haftorgane (Rhizoiden) zu bilden (Fig. 14). Die Rhizoiden sind stets farblos, dünner als die Luftmycelien und schwach verzweigt. Sie können sich verlängern, aber ohne Querwände zu bilden.

Die Hauptfäden der Stolonen und der daraus wachsenden Seitenäste können sich weiter verzweigen (Fig. 6); von sämtlichen Stolonen erheben sich Sporangienträger, jedoch nicht in konstanter regelmässiger Anordnung auf den Ausläufern, sondern sie sind einzig oder quirlig in einen Knoten vertheilt.

Der Stiel ist einfach, gabelig oder mehrfach deutlich sym-

podial (Schraubel und Wickel) verzweigt, jeder mit einem Sporangium versehen. Seine Länge variiert zwischen 90 und 100  $\mu$ ; er ist schwach bräunlich gefärbt. Manchmal kommt an dem Hauptstiel der Sporangienträger eine eigenthümliche Anschwellung vor, welche mit denjenigen von *Mucor Rouxii*,<sup>1)</sup>  $\beta$ - und  $\gamma$ -*Amylomyces*<sup>2)</sup> und *Mucor Cambodja*<sup>3)</sup> einige Aehnlichkeit besitzt. Dieses eigenthümliche Gebilde ist aber nicht anders als eine unvollständig entwickelte und schnell ausgekeimte Sporangienanlage (Fig. 9c und 10).

Die Sporangien sieht man nicht makroskopisch, selbst kaum mit Hilfe einer Lupe. Unter stärkerer Vergrößerung erkennt man die jungen Sporangien zuerst farblos, später hellgrau, dann immer dunkler werdend, bis sie schliesslich schwarzbraun sind. Sie sind kugelig oder auch oft etwas lang gestreckt, von verschiedener Grösse, meist vielsporig, aufrecht, am Träger sich öffnend. Die Sporangienwand ist glatt, zerbrechlich, an der Basis mit kleinen Fetzen der Sporangienwand—Basalkragen—versehen (Fig. 9–13). Eine vollständig entwickelte Columella ist von 15 bis 20  $\mu$  breit und 10–15  $\mu$  hoch, breit aufsitzend, halbkugelig, etwas braun; die Apophyse ist mehr oder minder deutlich vorhanden; die unmittelbar hinter der letzteren liegenden Theile sind mehrfach mit einer Querwand versehen. Nicht selten zeigen die zerbrochenen Sporangien die Columella mit einem dünnen, am Ende kugelig angeschwollenen Fortsatze (Fig. 15).<sup>4)</sup>

1) WEHMER, C., Die „chinesische Hefe“ und der sogenannte *Amylomyces* (= *Mucor Rouxii*). Centrabl. f. Bak. u. Paras., II. Abth., Bd. VI, p. 353.

2) LINDNER, P., Mikroskopische Betriebskontrolle in der Gährungsgewerbe. Dritte Auflage, P. 322.

3) CHRZASZCZ, T., Die „chinesische Hefe.“ (Centrabl. f. Bak. u. Paras., II. Abth., Bd. VII, p. 326).

4) In allen Nährböden entwickelt sich die zwergige Form der Sporangien. Sie ist kurz gestielt, sehr klein, mit zerbrechlicher glatter Membran; sporenarm, doch selten ganz frei von Sporen.

Die Sporen sind meist länglich, auch rund, in der Grösse fast gleichmässig (ca.  $3 \times 5$  oder  $3 \mu$  gross), dünn- und glattwandig und bräunlich gefärbt. In variabler Zahl füllen sie das Sporangium dicht und erscheinen in grösserer Anhäufung dunkelbraun (Fig. 16). Wie man im allgemeinen bei den Sporen der Mucorineen beobachtet, quellen sie vor der Keimung enorm auf, sodann erfolgt die Keimung mit sehr wenigen Ausnahmen an 2–5 Stellen durch Sprengen der Membran und Hervortreten des Keimschlauches. Wie BACHMANN<sup>1)</sup> bei *Morticella van Tieghemi* einmal beobachtete, geht die Volumenvergrösserung der Spore während des Mycelwachstums noch weiter fort, bis diese mit Fetttropfen beladen wird. In Objektträgerkulturen waren schon nach 24 Stunden die Stielgemmen an den Schlauchenden gebildet, später kamen die Sporangienträger (Fig. 17).

Gemmen kommen nicht selten vor, besonders reichlich an Flüssigkeitmycelien, niemals aber auf den Luftmycelien und Sporangienträgern. Sie sind von zweierlei Art, nämlich Kugelgemmen und Hyphengemmen; beide sind kugelig oder oval, aber oft auch unregelmässig gestaltet, stets farblos, mit dünner glatter Membran und glänzender Inhaltmasse. Die Grösse variiert von 5 bis  $25 \mu$ . Die Keimung geht schnell vor sich, eine hefeähnliche Sprossung wurde dabei nicht beobachtet (Fig. 5). Zygosporien konnten niemals gebildet werden.

## II. PHYSIOLOGISCHES.

Unsere *Tieghemella*-Art wächst wie andere Mucorineenarten günstiger auf festem Substrat als in flüssigem Nährboden; hier

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1) BACHMANN, P., *Morticella van Tieghemi* nov. sp. Beitrag zur Physiologie der Pilze. (Pringsheim Jahrb. f. wiss. Bot., Bd. 34, 1900, p. 279).

machen jedoch Würze und Kojidekokt eine Ausnahme, da in ihnen eine gut entwickelte Deckenbildung stattfindet.

Von festen Substraten sind Reis, Klebreis, Brot, Kartoffeln, Bohnen u. a. als die günstigsten zu nennen; auf ihnen wachsen graue Mycelien mit reichlichen Sporangien hoch in die Luft hinein, und, wie schon oben erwähnt, krümmen sich dann abwärts, bis sie in Kontakt mit dem Substrate kommen, um dort Rhizoiden zu bilden. Weniger günstig ist Nährgelatine, am schlechtesten Nähragar (sogar in optimaler Temperatur).

In Würze und Kojidekokt wächst der Pilz am üppigsten; aufangs entstehen submerse Mycelien, die schnell auf dem Flüssigkeitsniveau eine weisse Decke bilden. Die Letztere, in der Dicke allmählich zunehmend, lässt die Luftmycelien emporwachsen, welche spärliche Sporangienträger tragen, während die Flüssigkeitsmycelien reichliche Gemmen bilden. Wie bei *Mucor Rouxii*<sup>1)</sup> beruht der wachsthumsbegünstigende Einfluss der Würze (auch des Kojidekokts) nicht auf den Zuckerarten in der Flüssigkeit, sondern auf ihrer besonderen Zusammensetzung. Weil die Dextrose- und Maltoselösungen mit anorganischen Stickstoffsalzen ( $\text{NH}_4\text{NO}_3$ )<sup>2)</sup> für sich allein sehr schlechte Nährflüssigkeiten sind, entstehen hier nur submerse Mycelien (selten spärliche Deckenbildungen in Dextroselösung). Minder günstig sind Saccharose<sup>3)</sup>, Laevulose, Galaktose und Laktose.

In einer Reihe der Kulturen habe ich die Werthe verschiedener Stickstoffliefernden Substanzen<sup>4)</sup> verglichen, und gefunden, dass der Pilz mit Pepton, Asparagin und Tyrosin am üppigsten

1) WEHMER, C., Centralbl. f. Bak., Abth. II, Bd. VI, p. 353.

2) Von anderen Mineralstoffquellen sind  $\text{KH}_2\text{PO}_4$ ,  $\text{MgSO}_4$  und  $\text{Fe}_2\text{Cl}_6$  in der Kulturenlösung vorhanden.

3) Es wurde gefunden, dass Rohrzucker in reduzierenden Zucker gespalten wird.

4) Die Substanzen sind in 1% Verdünnung gebraucht, als Kohlenstoffquelle wandte ich 5% Dextrose an.

gedeiht; Harnstoff, Ammoniumsulfat, Ammoniumnitrat und Kaliumnitrat kommen als Nährstoffe in ihren Reihenfolge.

**Einfluss der Temperatur:** Ausser durch die Nährböden wird das Wachstum unseres Pilzes auch durch die Wärme stark beeinflusst. In 30–35°C entwickelt er sich nur langsam, selbst auf dem gut ernährenden Reis. Dagegen wächst der Pilz bei 20–25°C stets so rasch und üppig, dass eine gut ernährte Bodenfläche binnen wenigen Tagen mit Mycelien bedeckt wird.

**Färbungen:** Die in Zuckerlösungen vegetierenden Mycelien sind immer farblos. Anders ist es bei Kulturen auf festem Substrate, besonders auffällig auf Brot, Reis und Klebreis. Hier tritt eine schwarzbraune Färbung ein, sofern die Böden von den Pilzhypen bedeckt werden. Die Farbe entwickelt sich aber nur auf den Thermostatenkulturen (30–35°C), sie fehlt in Zimmertemperaturkultur, wo das Mycel die gewöhnliche graue Farbe zeigt. Der schwarzbraune Farbstoff liegt in der Hyphenwand.

**Stärkeverzuckerung:** Die Reispasta ändert sich nicht merklich bei der Pilzkultur, doch liess sich durch Versuch konstatieren, dass unserem Pilze das Vermögen für Stärkeverzuckerung zukommt.

**Gelatineverflüssigung:** Die Gelatineverflüssigung ist für unsere Art, wie bei anderen Mucorineenarten, so träge, dass man zum Erkennen des Wirkungsbeginns auf der Strichlinie eine mehrwöchentliche Kulturdauer benötigt.

### III. DIAGNOSE.

Rasen locker, grau; Stolonen farblos oder schwarzbraun, verzweigend. Rhizoiden fast unverästelt, stets farblos, nirgends mit Querwänden.



Sporangienträger geradständig, braun gefärbt, gewöhnlich unverzweigt, manchmal aber sympodial verästelt, und in letzterem Falle mit oder ohne Anschwellung (missgebildete Sporangium). Sporangien kugelig, oft in der Längsrichtung schwach verlängert, grau oder braun; reif schwarzbraun, aufrecht. Sporangienwand zerbrechlich, mit Basalkragen. Columella halbkugelig, breitauf-sitzend, mit glatter, brauner Membran, nicht selten mit einem Fortsatze. Zwerghaft entwickelte Sporangien vereinzelt. Sporen dunkelbraun, länglich oder kugelig. Gemmen stets reichlich, farblos, mit glatter farbloser Wand, meist kugelig oder oval. Zygosporen und Kugelhefen fehlen.

Wächst gut auf Reis, Klebreis, Brot, Kartoffeln, Bohnen, Nähr-gelatine, Würze und Kojidekokt; am schlechtesten auf Agar und Laktose, verzuckert Stärke, verflüssigt Gelatine nach längerer Zeit, färbt gedämpften Reis, Klebreis und Brot schwarzbraun.

#### Grössenverhältnisse :

Höhe des Kulturrasens.	1-2 cm.
Stolonendurchmesser	9 $\mu$ .
Rhizoidendurchmesser	7 $\mu$ .
Sporangienträger {	Höhe 90-400 $\mu$ .
	Dicke 4-8 $\mu$ .
Sporangindurchmesser	20-22 $\mu$ .
Columella	15-20 $\mu$ breit und 10-15 $\mu$ hoch.
Sporengrösse	5 $\times$ 3 oder 3 $\times$ 3 $\mu$ .
Gemmengrösse	5-25 $\mu$ .

Fundort: In einer Luftprobe des Gährkellers der Sake-brauerei zu Stadt Handa, Provinz Owari (Februar 1903).

#### Affinität:

Fasst man die oben erwähnten Eigenschaften des Pilzes zu-sammen, so ist er von allen bislang beschriebenen verschieden. Obschon *Tieghemella Orchidis* mit den vorstehenden Art viele Aehnlichkeit besitzt, unterscheidet sie sich dadurch, dass sie stets einfache oder einmal sich verzweigende Sporangienträger bildet,

während bei *T. japonica* mehrfache sympodiale Verzweigung auftritt. Ausserdem zeigt die Sporangienwand der *T. Orchidis* eine sehr feine körnige Inkrustation, welche bei *T. japonica* nie zum Vorschein kommt.

Was den Fortsatz der Columella betrifft, so ist er bei *T. japonica* stets am Ende kugelig angeschwollen, jedoch bei *T. Orchidis* nicht beständig und ungleich gestaltet. Die Sporen beider Arten zeigen ebenfalls eine verschiedene Gestalt, bei *T. Orchidis* sind sie stets kugelig, bei *T. japonica* kommen kugelige und ellipsoidisch-ovale Formen vor. Eine merkwürdige Verschiedenheit besteht auch darin, dass die Quellung der Sporen bei der Keimung nur an Sporen von *T. japonica* vorkommt.

Juni 1903.

Botanisches Institut, Kaiserl.

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**K. SATTO.**  
TIEGHEMELLA JAPONICA.

TAFEL

## Erklärung der Tafel.

- Fig. 1 ( $\times 25$ ). Hyphen mit Sporangienträger (Reiskultur).  
Fig. 2 ( $\times 400$ ). Sporangienträger und Rhizoiden (Brotkultur).  
Fig. 3 ( $\times 125$ ) (*a-c*). Rhizoiden (Brotkultur).  
Fig. 4 ( $\times 400$ ). Rhizoid, stark vergrößert (Brotkultur).  
Fig. 5 ( $\times 400$ ). Gemmen aus Zuckerlösung.  
Fig. 6 ( $\times 560$ ). Verzweigung der Stolonen (Brotkultur).  
Fig. 7 ( $\times 400$ ). Substratmycelium (Gelatinekultur).  
Fig. 8 ( $\times 400$ ). Dasselbe mit stark unregelmässiger Kontour und einer Querwand (*q*) (Brotkultur).  
Fig. 9 ( $\times 400$ ) (*a-e*). Verschiedene Formen der verzweigten Sporangienträger (aus verschiedenen Kulturen).  
Fig. 10 ( $\times 400$ ) (*a-d*). Entwicklungsstadien der Anschwellung an den Sporangienträgern (Brotkultur).  
Fig. 11 ( $\times 400$ ) (*a, b*). *a* normales, *b* zwergiges Sporangium (Gelatinekultur).  
Fig. 12 ( $\times 400$ ). Eine Reihe der zwergig gebildeten Sporangien (Gelatinekultur).  
Fig. 13 ( $\times 400$ ) (*a-d*). Entwicklungsstadien der Sporangien (Reiskultur).  
Fig. 14 ( $\times 400$ ) (*a, b*). Entwicklungsstadien des Rhizoides (Brotkultur).  
Fig. 15 ( $\times 400$ ) (*a-c*). Columella. *a, b* normal, *c* mit Fortsatz (Reiskultur).  
Fig. 16 ( $\times 560$ ). Sporen (Reiskultur).  
Fig. 17 ( $\times 560$ ) (*a-c*). Sporenkeimung. *a* Beginn; *b* etwas weiterer Fortschritt; *c* 24 Stunden nach der Keimung, mit Gemme (*g*) und Sporangiumanlage (*s*) (Tropfenkultur).





## Jurassic Ammonites from Echizen and Nagato.

By

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*With 4 plates.*

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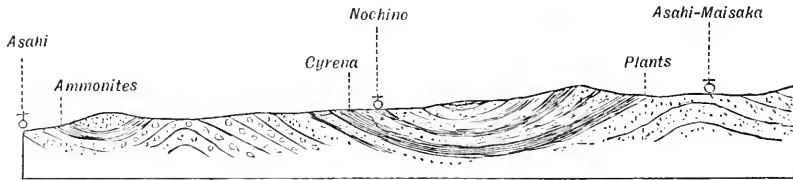
### A. Ammonites from Echizen.

The occurrence of Ammonites in the Jurassic plant-bearing series of the province of Echizen was known as early as 1882, when Dr. KOCHIBE discovered them in a shale near the village of Shimoyama in the same province. No collection of them, however, was made, until Mr. M. MATSUSHIMA, after a careful search near Kaizara and its vicinity in 1885 succeeded in finding several specimens which were afterwards deposited in the museum of the Science College of the Tokyo University. The results of the study of these fossils are as follows.

According to Mr. MATSUSHIMA, the rock-layers exposed along the river Ishidoshiro, a branch of the Ananogawa in the district of Ono, consist of a basal conglomerate and a complex of shales and sandstones. This complex is divided by him into three parts, the *Lower* or *Ammonite-bed*, the *Middle* or *Plant-bed* and the *Upper* or *Cyrena-bed*. It is in this *Ammonite-bed* that the above fossils were found. The chief locality for them is Horadani near

the village of Kaizara, but there are also two other localities, viz., Nagano and Shimoyama which in a direct line are not quite 4 kilometers from the first named place.

The following is a profile along the river Ishidoshiro, as given by Mr. MATSUSHIMA in his geological paper on Echizen (MS).



As might be expected from the mostly freshwater nature of the Jurassic formation of Echizen, the Ammonite remains are of very rare occurrence. Moreover their preservation is such as to make their determination very difficult, the specimens being generally flattened by rock-pressure.

The following are the names of species which I have been able to distinguish in these Ammonites :

1. *Perisphinctes* (*Procerites*) *Matsushimai* nov. sp.
2. *Perisphinctes* (*Grossouvria*) *Hikii* nov. sp.
3. *Perisphinctes* (*Biplices*) *kaizaranus* nov. sp.
4. *Perisphinctes* (*Biplices* ?) *Kochibei* nov. sp.
5. *Perisphinctes* (*Ataxioceras*) sp.
6. *Oppelia echizenica* nov. sp.

Of the five species of *Perisphinctes*, four are new, and the remaining one is also probably so, although at present this is uncertain. They are, excepting *Perisphinctes Hikii* which shows some relation to a Kelloway species, *Perisphinctes Steinmanni* PAR. ET BON., all more or less allied to the foreign Oxford



forms; viz. *Perisphinctes Matsushimai* to *Perisphinctes promiscuus* BUKOW., *Perisphinctes kaizaranus* to *Perisphinctes triplex* QUENST., and *polygyratus* REIN., *Perisphinctes Kochibei* to *Perisphinctes subcolubrinus* WAAG., and *Perisphinctes* sp. to *Perisphinctes occultefurcatus* WAAG. The only other Ammonite beside *Perisphinctes* is a new form of *Oppelia* which exhibits a distant relationship to *Oppelia nobilis* NEUM. of the Tithonian. Therefore it is hardly to be doubted that we have here a bed which must be ascribed to the Malm. This assertion is also strengthened by the preponderance of *Perisphinctes* which has its greatest development in the same formation. To what part of the Malm this Ammonite-bed belongs is at present difficult to say, but probability points to its lower part or Oxford.

The determination of the Echizen Ammonites as those of the Malm leads to the important conclusion that the plant-bearing series developed in that part of Japan is not, as formerly believed, entirely Middle Jurassic, but that a part of it represents also the upper portion of the same formation.

## DESCRIPTION OF THE SPECIES.

### 1. **PERISPINCTES (PROCERITES) MATSUSHIMAI** M.

Pl. I. Fig. 1.

The shell is compressed, discoidal, widely umbilicated, consisting of about 6 whorls which are nearly  $\frac{1}{2}$  involute. The whorls are also laterally compressed, being only slightly convex. They are furnished with many rigid elevated ribs separated by smooth intervals of a much greater breadth. These ribs are

tolerably sharp in the inner whorls, but become gradually obtuse towards the mouth. They rise at the umbilical suture, are directed a little forward and divide into three smaller ones near the venter into which they seem to pass in a straight line. In the last and the next to the last whorls, there are two deep grooves which are more oblique than the ribs and separated from each other by about one-half the length of the whorl.

The diameter of the shell in our only specimen is 138 mm. with an umbilical width of about 77 mm., so that the ratio of the two is 10 to 5.7. But as the specimen is somewhat distorted, the real umbilical width may be a trifle less.

The number of ribs in one half of the last whorl is 28, so that the whole number may be about 55.

The suture line seems to be deeply incised, although it is not distinctly visible.

This species shows a great resemblance to *Perisphinctes promiscuus* BUKOWSKI (*Ueber die Jurabildungen von Czenstochau in Polen*, p. 308, pl. IV., fig. 1, pl. V., figs. 1, 2) of the Lower Oxford of Poland. The only difference which I could find in the surface markings of the two is in the number of ribs which in the Polish species is said to be 50. The shape of the whorls can not be well compared, as our specimen has been subjected to rock-pressure; but as far as I can judge from the general outline of the shell, the Japanese form appears to have a laterally more compressed whorl than the Polish one, in which it is said to be ovate in section.

*Perisphinctes promiscuus* occurs also in the Lower Oxford of France and Portugal.

Locality :—Nagano, in a hard dark-coloured shale.

2. **PERISPINCTES (GROSSOUVRIA) HIKII** M.

Pl. I. Figs. 2, 3.

There are two specimens belonging to this species which may be characterized as follows:

Shell flatly discoidal, with a wide umbilicus. Whorls numerous, very slightly involute, oval slightly higher than broad, transversely ribbed. Ribs numerous, elevated, with the upper edge obtuse, and showing the characters of the *Curvicosta* type, that is to say, rising at the umbilical suture, they are at first directed obliquely forward, but near the middle of the flanks bend backward and then bifurcate, the ribs arising from bifurcation going over straight to the venter. The division of ribs usually takes place near the external margin of the whorl, but sometimes a little lower. Now and then there are simple ribs between the divided ones. Number of ribs 43-45.

The larger of the two specimens shown in fig. 2 is pressed flat on the stone, especially near the mouth. It measures about 39 mm. in diameter, that of the umbilicus being 20 mm. The other specimen (fig. 3) which is better preserved shows the diameter of the shell 25 mm. and that of the umbilicus 11 mm. Therefore the umbilical width varies between 0.44 and 0.51.

The suture-line is unknown.

The hitherto described species to which the Japanese form can be compared is *Perisphinctes Steinmanni* PARONA and BONARELLI (*Sur la faune du callovien inférieure de Savoie*, pl. IX, fig. 2) of the Italian Kelloway which, according to Siemiradzki, is identical with *Perisphinctes Bucharicus* NIKITIN (*Notes sur les dépôts jurassiques de l'Himalaya et de l'Asie Centrale*, pl. I,

*figs. 1-4*). But our species has a larger umbilicus and closer ribs.

Locality :—Kaizara, in a dark micaceous shale.

### 3. **PERISPINCTES (BIPLICES) KAIZARANUS** M.

Pl. I. Fig. 4.

The compressed, discoidal shell shows a wide umbilicus which is slightly deepened. The whorls are a little less than one-half involute, ovate in section, somewhat higher than broad and ornamented with numerous, elevated but obtuse, rigid, radial ribs separated by interspaces of a like breadth. These ribs which number about 50 on the last whorl generally split into two a little higher than the middle of their lengths, but occasionally there is a simple rib between. There are also two deep grooves in the last whorl, the one near the mouth and directed obliquely forward, and the other diametrically opposite the first one and directed radially. In the inner whorls too such grooves seem to have been present, as the third is seen diametrically opposite the second. The suture-line is unknown.

We have only a single specimen of this species which shows the following dimensions :

Diameter of shell	...	...	...	...	35 mm.
Umbilical width	...	...	...	...	0,54
Thickness of whorl	...	...	...	...	0,26
Height above umbilical suture	...	...	...	...	0,33

Our fossil shows many relations to *Perispinctes subcolubrinus* WAAGEN (*Jurassic Fauna of Katch*, p. 180, pl. XLIX., fig. 3), an Oxford species found in India, Poland and Portugal. But

beside the size of the shell, the whorls are rounder and the ribs directed a little forward in the latter species.

Locality :—Kaizara, in a dark micaceous shale.

#### 4. **PERISPINCTES (BIPLICES ?) KOCHIBEI** M.

Pl. I. Fig. 5.

The single specimen, probably from Shimoyama, shows a compressed, discoidal shell about 50 mm. in diameter, with umbilical width of about 22 mm. The whorls are laterally compressed and only very little convex, the umbilical wall being almost perpendicular. The transverse ribs are numerous, radial, generally rigid, elevated but obtuse, about 38 in the last whorl, separated by intervals usually about twice as broad as the ribs themselves, but sometimes less. These ribs bifurcate either at half their lengths or a little higher up, and between the riblets thus formed there is commonly a simple free rib, so that the main ribs appear as if split into three. In a rare case the simple rib reaches down to the edge of the umbilicus and assumes the appearance of a main rib with the intervals with the neighboring ones much narrower than in other cases. The shape of the venter can not clearly be made out, but it seems to have been more or less rounded.

Suture-line unknown.

Our species shows a close relationship to *Perisphinctes triplex* QUENSTEDT and *Perisphinctes polygyratus* REINECKE of the Oxford formation. The main difference, if we set aside the shape of the whorl which is at present uncertain, appears to be the irregularity of ribs in the Japanese form.

5. **PERISPINCTES (ATAXIOCERAS) SP.**

Pl. I. Fig. 6.

A single specimen from Kaizara, not quite perfect, shows a flat discoidal shell with a wide umbilicus and numerous volutions which are about  $\frac{1}{2}$  involute. The whorls are oval in transverse section, slightly higher than broad, with convex lateral sides and steep umbilical wall. The transverse ribs which rise at the umbilical suture number about 34 in the last whorl, and are nearly radial in the same whorl, while in the inner ones they are directed obliquely forward. These ribs are more or less rigid and sharp, and split into two at half their length or a little more.

The diameter of the shell measures 40 mm. and that of the umbilicus 19 mm.

Our species much resembles *Perispinctes occultefurcatus* WAAGEN from Katch (*Jurassic Fauna of Katch*, p. 195, pl. XL., fig. 4). But as the venter in our specimen is not well preserved it is not possible to determine whether there is a shallow dorsal groove as in the Indian species. Moreover the ribs are somewhat less in ours.

6. **OPPELIA ECHIZENICA M.**

Pl. I. Fig. 7.

A single specimen of a strongly compressed, discoidal, keeled shell, about 31 mm. in diameter with an umbilical width of about 12 mm. The whorls are laterally compressed and only slightly convex, apparently without any ribs, the only ornamentation being a row of distant nodes which bounds the keel on both sides and

which disappear in the last one fourth of the last whorl. The umbilical wall is nearly perpendicular with the edge more or less angulated. Body-whorl about  $\frac{3}{4}$ .

The several irregular transverse grooves seem to be accidental characters caused by rock-pressure.

The suture-line is only partly visible. It consists of deeply toothed lobes and saddles.

As an *Oppelia* this species shows a comparatively wide umbilicus, recalling in this respect *Oppelia nobilis* NEUM. of the Tithonian of Transylvania and Switzerland.

Locality :—Kaizara, in a micaceous shale.

### B. Ammonites from Nagato.

The first discovery of Ammonites in the province of Nagato is attributed to a certain school-master, KIMURA by name, who, in 1887, is said to have noticed them in a new road-cutting near Nishi-Nakayama in the district of Toyora. But they were not known to the scientific world, until they were collected by Mr. K. INOUE in 1895.

At present, the fossils are known from two places very near to each other, namely, Nishi-Nakayama and Ishimachi, the discovery in the latter place being due to Mr. OKADA who visited the district in 1899. In both places they occur in a clayslate, which at Nishi-Nakayama has been weathered into a soft yellowish shale. The preservation must be called imperfect, as the fossils have been almost without exception pressed flat on the stone, making their determination extremely difficult.

The Ammonite-bearing slate belongs to the so-called *Inkstone Series* which overlies the Rhætic plant-bed of the neighboring district. The series consists of thick layers of clayslates, sandstones and conglomerates which, in the upper part, contain strata of schalstein and which, therefore, have been distinguished by Mr. INOUE into the *Upper* or *Schalstein-bearing Part* and the *Lower* or *Non-Schalstein Part*. It is in this lower part that the above Ammonites occur.

The species of Ammonites hitherto found at Nishi-Nakayama and Ishimachi are as follows :

1. *Hildoceras chrysanthemum* nov. sp.
2. *Hildoceras densicostatum* nov. sp.
3. *Hildoceras Inouei* nov. sp.
4. *Grammoceras* (?) *Okadai* nov. sp.
5. *Harpoceras* sp.
6. *Harpoceras* sp.
7. *Celoceras subfibulatum* nov. sp.
8. *Dactylioceras helianthoides* nov. sp.

Besides, there is an impression of a large *Aegoceras*-like Ammonite, together with flat *Mytilus*-like bivalves.

Of the eight species of Ammonites above mentioned, *Hildoceras chrysanthemum* bears a close relationship to *Hildoceras boreale* SEEBACH of the Upper Lias, while the two other *Hildoceras* are more or less allied to the first. Of the two *Harpoceras* not specifically determined, the one shows a great resemblance to *Harpoceras Lythense* YOUNG also of the Upper Lias. *Celoceras subfibulatum* and *Dactylioceras helianthoides* resemble respectively *Celoceras fibulatum* and *Dactylioceras annulatum*, both described by WRIGHT from the Upper Lias of England. From these facts it is clearly to be seen that we have here a



formation which undoubtedly belongs to the Lias, and indeed to its upper part.

There seem to be several horizons in the Ammonite-bearing layers. Mr. INOUE speaks of three such as existing at Nishi-Nakayama, while Mr. OKADA mentions only two from Ishimachi. It is to be hoped that future investigations will throw more light on this subject.

## DESCRIPTION OF THE SPECIES.

### 1. **HILDOCERAS CHRYSANTHEMUM** M.

Pl. II. Figs. 1-4.

The shell is discoidal, very much compressed, carinated and widely umbilicated, with the umbilical wall very steep or nearly perpendicular. The whorls are narrow and only very slightly involute, with lateral sides flat and furnished with numerous, broad, obtuse, sigmoidal ribs separated by valleys of a like breadth. These ribs become flatter and less prominent toward the mouth, and where they bend backward, which takes place at about  $\frac{1}{3}$  their length from the umbilical edge, the surface of the whorl is marked by a shallow depression which is most distinct in the last half of the last whorl. Body-chamber about  $\frac{1}{4}$ . The external saddle is broader than the external lobe, and divided into two unequal parts by a shallow incision; the external lobe is quite simply incised, the incisions being pointed.

The specimen shown in fig. 1 is the best preserved, and one of the largest. Its diameter measures 84 mm., with an umbilical width of 40 mm. The ribs number 43 in the last whorl,

and are accompanied by fine sigmoidal lines which are especially numerous in the valleys near the mouth. In young specimens (figs. 2, 3) the general characters of the ribs are the same, but their number is less, being at most 40; the sigmoidal striae are often more distinct.

The keel is sharp and bounded by a furrow on each side, but as our specimens have all been subjected to rock-pressure, its exact shape can not be made out.

In one of the fragments of a large shell, there was found an impression of aptychus (fig. 4) marked by oblique ribs between which there are several oblique striations, so that it looks not unlike the one figured by WRIGHT (*Lias Ammonites*, pl. LXI, fig. 4).

Our species is closely allied to a shell figured by WRIGHT as *Ammonites Levisoni* (*Lias Ammonites*, p. 438, pl. LXI, figs. 5, 6) which, according to HAUG, is not a true *Ammonites Levisoni*, but *Ammonites borealis* SEEBACH (*Der Hannoversche Jura*, p. 150, pl. VII., fig. 5), both of which occur in the Upper Lias of Europe. The Japanese form, however, differs from *Ammonites borealis* as figured by SEEBACH in having a steep umbilical wall and more deeply incised suture-line, in which latter respect it resembles *Ammonites Levisoni* as figured by WRIGHT in his fig. 3, pl. LXI. Anyhow it must be looked upon as a species strongly akin to these European forms.

Locality:—Nishi-Nakayama and Ishimachi; tolerably frequent.

## 2. **HILDOCERAS DENSICOSTATUM** M.

Pl. III. Figs. 1, 2.

Shell discoidal, compressed, keeled, widely umbilicated; whorls compressed, flat, scarcely involute, with umbilical edge rounded

and umbilical wall perpendicular, ornamented with thickly set, obtuse, sigmoidal ribs separated by valleys mostly narrower, and in adult specimens running out in numerous, unequal, sigmoidal striae near the mouth; the place where ribs bend backward is marked with a slight depression; keel sharp, bounded on each side by a furrow.

This species is closely related to the preceding one from which it is distinguished by a greater number of ribs. In a specimen (fig. 2) which measures 63 mm. in diameter, their number is about 53, while in one with the diameter of 48 mm. there are about 55 of them in the last whorl. Fig. 1 shows the largest specimen, 90 mm. in diameter and with ribs near the mouth splitting into many finer ones. The proportion of the shell-diameter to the umbilical width is about 10 to 4.

Locality :—Nishi-Nakayama and Ishimachi; quite frequent.

### 3. **HILDOCERAS INOUYEI** M.

Pl. II. Figs. 5, 6.

The shell is discoidal, much compressed, keeled, with a narrow umbilicus, its breadth being about  $\frac{1}{3}$  or a little less of the shell-diameter. Involution about  $\frac{1}{3}$ . The whorls are flat with obtuse sigmoidal ribs whose number varies between 40 and 60 according to age. The umbilical wall is perpendicular, with its edge rounded. Keel high and sharp, and bounded by a channel on each side.

This species resembles the two preceding in the shape and surface markings of the shell, but is decidedly more narrowly umbilicated.

Most of the specimens are small, the largest complete one (fig. 6) being 40 mm. in diameter with an umbilical width of 11 mm., and bearing about 58 ribs. There are however fragments of larger shells which seem to have attained over 50 mm. in diameter. A small specimen (fig. 5) 25 mm. in diameter has an umbilical width of about 8 mm. and some 40 ribs.

Locality :—Frequent at Nishi-Nakayama; less so at Ishimachi.

#### 4. **GRAMMOCERAS (?) OKADAI** M.

Pl. IV. Fig. 3.

We have a single specimen of a compressed, discoidal, keeled shell, about 35 mm. in diameter and with an umbilical width of about 10 mm. The whorls are laterally very flat, with a steep umbilical wall and obtuse umbilical edge, and ornamented with about 60 fine S-shaped obtuse ribs, separated by intervals of a like breadth. The keel is sharp and bounded by shallow channels.

This form resembles in its outer sculpture *Grammoceras acutum* TATE (WRIGHT, *Lias Ammonites*, pl. LXXXVII., fig. 7) of the English Upper Lias, which seems to have more convex lateral sides.

Locality :—Nishi-Nakayama.

#### 5. **HARPOCERAS** sp.

Pl. IV. Fig. 1.

A flat, compressed, keeled shell, nearly 90 mm. in diameter, with the umbilicus 24 mm. wide. The whorls are laterally flattened and furnished with about 43 flat sigmoidal ribs, separated

by intervals of nearly a like breadth. The edge of the umbilicus is nearly right-angled, and its wall perpendicular, so that if the inner whorls were preserved in our specimen, they would appear descending stair-like into their centre.

The general form, the mode of costation and the small umbilicus with perpendicular walls make our species resemble *Harpoceras Lythense* YOUNG and BIRD (WRIGHT, *Lias Ammonites*, p. 444, pl. LXII., figs. 4-6) of the English Upper Lias; but how far the resemblance extends, it is at present not possible to make out from the imperfect state of preservation of our fossil.

Locality :—Nishi-Nakayama.

## 6. **HARPOCERAS** SP.

Pl. IV. Fig. 2.

This is another flat, keeled, narrowly umbilicated shell, about 85 mm. in diameter, and with an umbilical width of 20 mm. The ribs are sigmoidal as in the preceding species, but decidedly denser and more numerous, the number reaching up to 70, and near the mouth running out into many sigmoidal striations. The umbilical wall is perpendicular.

The form and outer sculpture show a great resemblance to *Harpoceras exaratum* WRIGHT (*Lias Ammonites*, p. 441, pl. LXII., figs. 1-3) of the Upper Lias.

Locality :—Nishi-Nakayama.

## 7. **CÆLOCERAS SUBFIBULATUM** M.

Pl. III. Figs. 3-6.

There are several specimens of a *Cæloceras* which may be characterized as follows :

The shell is discoidal, compressed, and very widely umbilicated. The whorls are scarcely involute, laterally a little convex, externally rounded, with a steep umbilical wall and obtuse umbilical edge. They are transversely ribbed, the ribs being numerous (about 50 in number in a shell 50 mm. in diameter), radial, straight or slightly concave toward front, sharp, elevated, either simple, or united in twos by a knob near the venter forming the so-called "loop and button style," whence they again separate into two on the venter. The intervals between the ribs are wider than the ribs themselves. The proportion of the shell-diameter to the umbilical width is about 5 to 3.

The transverse section of a whorl can not be clearly made out, owing to the rock-pressure to which the shell has been subjected; but as far as can be judged from several specimens, it seems to have been oblong.

The general shape of the shell and the manner in which the ribs are joined bring our species close to *Celoceras fibulatum* WRIGHT (*p.* 476, *pl.* LXXXV., *figs.* 5-11) of the Upper Lias, from which however it seems to differ in having ribs sometimes concave toward the front and the body-whorl a little lower, in which latter respect it more closely resembles *Celoceras subarmatum* YOUNG.

Locality :—Ishimachi and Nishi-Nakayama; not rare.

#### 8. **DACTYLIOCERAS HELIANTHOIDES** M.

Pl. IV. Figs. 4-6.

Several specimens of this neat Ammonite have been obtained, both from Nishi-Nakayama and Ishimachi, though in a more or less crushed condition.

The shell is flatly discoidal, and widely umbilicated, the umbilicus occupying about  $\frac{1}{2}$  of the shell-diameter. The whorls are only slightly convex on the lateral sides, while rounded on the external side or venter, with the umbilical edge obliquely sloping to the umbilical suture. Involution about  $\frac{1}{2}$  or a little less. The transverse ribs which rise at the umbilical suture are numerous, fine, elevated, radial, somewhat flexuous, regularly bifurcating in the inner whorls at about  $\frac{2}{3}$  their lengths, often remaining simple in the body-whorl. In this latter case, a short loose rib may be intercalated between two long simple ones, beginning free near the place where bifurcation usually takes place and going over to the venter. The number of ribs varies according to age, and also according to the individuals. In a shell 60 mm. in diameter (fig. 4), there are 80-90 ribs, while in one 45 mm. in diameter (fig. 5) we count about 60. The interspaces are flat and two to three times broader than the ribs themselves. In a specimen shown in fig. 6 which represents one-half of a shell nearly 70 mm. in diameter, the ribs are not so close together as in those above mentioned. Still I believe it belongs to the same species.

This form is closely related to *Dactylioceras annulatum* WRIGHT (*Lias Ammonites*, p. 475, pl. LXXXIV., figs. 7-9) of the English Upper Lias. But the latter has more numerous (up to 130), and flatter straight ribs.







**M. YOKOYAMA.**

JURASSIC AMMONITES FROM ECHIZEN AND NAGATO.

PLATE I.

## Plate I.

Fig. 1. *Perisphinctes (Proccrites) Matsushimai* n. sp.

Figs. 2, 3. *Perisphinctes (Grossouvria) Hikii* n. sp.

Fig. 4. *Perisphinctes (Biplices) kaizaranus* n. sp. 4a transverse section of a whorl.

Fig. 5. *Perisphinctes (Biplices ?) Kochibei* n. sp.

Fig. 6. *Perisphinctes (Ataxioceras)* sp.

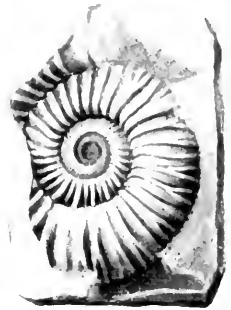
Fig. 7. *Oppelia echizenica* n. sp. 7a transverse section of a whorl.

*Fig. 1.*

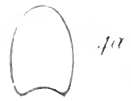
*Fig. 2.*



*Fig. 6.*

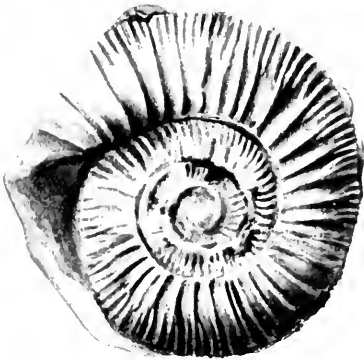


*Fig. 3.*

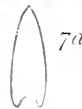


*Fig. 4.*

*Fig. 5.*



*Fig. 7.*





**M. YOKOYAMA.**

JURASSIC AMMONITES FROM ECHIZEN AND NAGATO.

PLATE II.

**Plate II.**

- Figs. 1-4. *Hildoceras chrysanthemum* n. sp. 1a part of the suture-line.  
4 showing an impression of one-half of the aptychus.  
Figs. 5, 6. *Hildoceras Inouyei* n. sp.

Fig. 5.

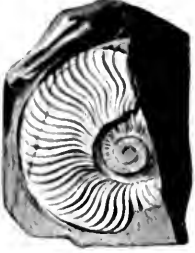


Fig. 1a.



Fig. 6.

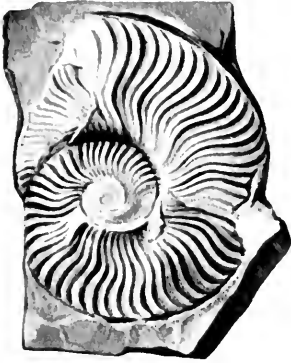


Fig. 4.



Fig. 1.



Fig. 2.

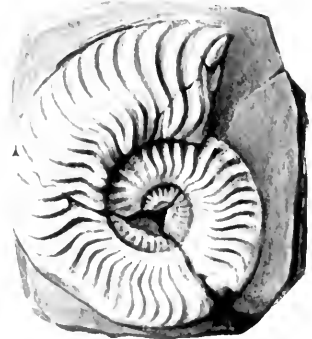


Fig. 3.







M. YOKOYAMA.

JURASSIC AMMONITES FROM ECHIZEN AND NAGATO.

PLATE III.

**Plate III.**

Figs. 1, 2. *Hildoceras densicostatum* n. sp.

Figs. 3-6. *Cæloceras subfibulatum* n. sp.

*Fig. 1.*



*Fig. 3.*



*Fig. 4.*



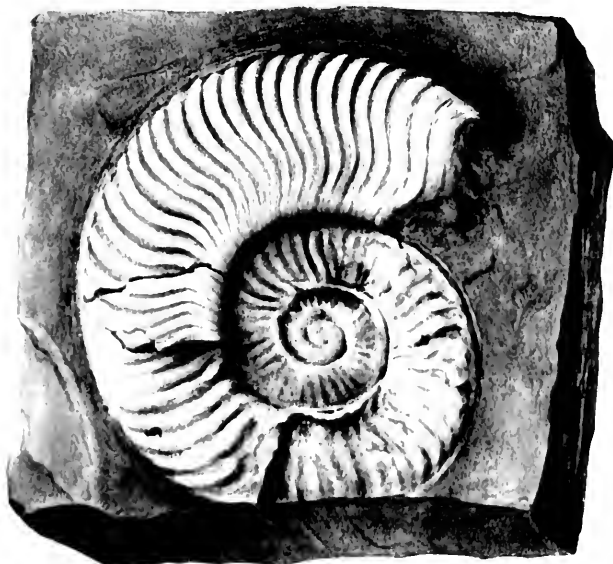
*Fig. 5.*



*Fig. 6.*



*Fig. 2.*



**Plate IV.**

Fig. 1. *Harpoceras* sp.

Fig. 2. *Harpoceras* sp.

Fig. 3. *Grammoceras* (?) *Okadai* n. sp.

Figs. 4-6. *Dactylioceras helianthoides* n. sp.

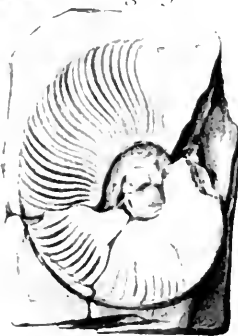


*Fig. 1.*

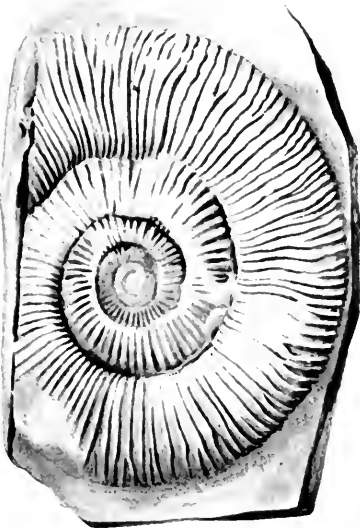


*Fig. 2.*

*Fig. 3.*



*Fig. 6.*



*Fig. 4.*



*Fig. 5.*













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